THE CHEMISTRY OF CARBENE AND CARBONYL COMPLEXES OF PLATINUM

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THESIS

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ABSTRACT

An extensive series of electroneutral alkoxy(organo)carbene complexes of platinum(II) has been prepared, the compounds having been characterised by elemental analysis, ^{1}H and ^{31}P n.m.r. and ir. spectroscopies and, in the case of cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$, by X-ray crystal structure determination.

The complex cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ reacted with CD_3OD via rapid H/D exchange of its benzyl $-CH_2-$ hydrogens, no alkoxy group exchange being observed. Reaction with dimethylamine proceeded by proton abstraction to give an alkoxy-vínylplatinum complex. These reactions have been compared with those of cationic alkoxy(organo)carbene complexes.

Reaction with chloride ions involved elimination of alkyl chloride, and produced the chloride-bridged complexes $[Pt_2(\mu\text{-}Cl)_2(COCH_2R)_2(PR'_3)_2]$. These complexes, as well as terminal carbonyl species, were also produced by thermolysis of the electroneutral carbene complexes.

Treatment of the neutral carbene complexes with tertiary phosphine produced acylbis(tertiary phosphine)platinum complexes, but if the reaction was performed in the presence of $AgSO_3CF_3$ the cationic carbene complexes, trans-$[PtCl\{C(OR")CH_2R\}(PR'_3)_2]^+ SO_3CF_3^-$, could be isolated. These derivatives were also prepared by alkylation of trans-$[PtCl(COCH_2R)(PR'_3)_2]$ species. Addition of $AgSO_3CF_3$ to the complexes cis-$[PtX_2\{C(OR")CH_2R\}(PR'_3)]$ produced dimeric, cationic carbene complexes, which reacted further by alkylation of the $SO_3CF_3^-$ anion.

The aroylplatinum complex, $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, was found to exist in solution in equilibrium with one isomer of $[PtClPh(CO)(PMePh_2)]$ (I). The other two isomers (II and III) were

produced by passing CO through a solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ but both were resistant to attempts to promote carbonyl insertion. The three isomers were identified by ^1H, ^{13}C and ^{31}P n.m.r. spectroscopy, and I was shown to have Ph and $PMePh_2$ in mutually trans-positions. Reaction of cis-$[PtCl_2(CO)(PMePh_2)]$ with $HgPh_2$ at low temperature produced I only which, on warming, equilibrated with $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)]$ (IV).

The I/IV equilibrium position for the complexes $[Pt_2(\mu\text{-}X)_2(COR)_2L_2]$ was shown to be dependent on the natures of R, X and L. The halide-bridged dimer was favoured by strong bridging ligands X, while the position of equilibrium was dependent on the electronic nature and, for bulky ligands, the size of the neutral ligands L. Thermodynamic parameters were obtained for the complexes $[Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$ (R = Et, Me or Ph), though the dependence of the equilibrium position on the nature of R is not understood. These results are suggested to be consistent with an alkyl or aryl migration mechanism for the CO insertion reaction.

The novel trans-$[PtX_2(CO)L]$ complexes have been prepared and characterised by ^{13}C and ^{31}P n.m.r. spectroscopies. They isomerised spontaneously to their cis-isomers, and the isomerisation could be catalysed by the addition of CO, X^- or L. The isomerisation process was shown to involve free CO. The interconversion of $[PtClPh(CO)(PMePh_2)]$ (II and III) also involved CO elimination, but was inhibited by excess CO. Possible isomerisation pathways have been proposed, and the mechanisms of isomerisation reactions of platinum complexes in general have been discussed. The halide-bridged dimers, $[Pt_2(\mu\text{-}X)_2R_2(PR'_3)_2]$ (R = Ph, acyl or aroyl), exist in solution as cis- and trans-isomers and a mechanism for their interconversion, involving reversible cleavage of one platinum-halide bridge bond, has been presented.

The ^{13}C and ^{31}P n.m.r. data for all the carbonyl, acyl and aroyl, and halide-bridged complexes have been tabulated, and the effects of the cis- and trans-ligands on chemical shifts and coupling constants have been discussed. Assignments of cis- and trans-geometries for the halide-bridged complexes have been made on the basis of solvent-dependence. The signs of the $^{1}J(Pt-C)$ and $^{2}J(P-C)$ coupling constants were determined for a typical member of each series of carbonyl complexes.

The results of crystal structure determinations for the complexes cis-$[PtCl_2(PEt_3)L]$ (L = CO, $P(OPh)_3$ and $P(NMe_2)_3$) were discussed, and both cis- and trans-influences of L were found to be significant. An X-ray structural investigation of trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ permitted some comparison of the relative importance of trans-influence in mono- and binuclear complexes to be made.

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CHAPTER ONE

Introduction

Development of organotransition metal chemistry.

The field of organometallic chemistry is one which has developed enormously over the last thirty years, yet it has its origins in the nineteenth and early twentieth centuries. The first organometallic compound was prepared by Zeise[1] in 1827. This complex, which has come to bear his name, contains a platinum-olefin bond and has the formula $K[PtCl_3(C_2H_4)]$, although its structure was not known at that time. The first organometallic compounds to be recognised as such were the zinc alkyls prepared by Frankland[2] in 1849. While attempting to produce ethyl radicals he heated ethyl iodide to 150°C in the presence of metallic zinc and obtained white crystals, which he correctly identified as ethylzinc iodide. By using diethylzinc, which Frankland also isolated, Buckton[3] was able to prepare diethylmercury, tetraethyl-lead and tetraethyltin.

The organometallic chemistry of magnesium was investigated by Grignard, and in 1900 was published[4] his work on organomagnesium halides or, as they are commonly called, Grignard reagents. In the ensuing years came the discoveries, notably by Schlenk and Ziegler, of the alkali metal alkyls,[5] including alkyllithium compounds.[6] These were to play an important role in organic synthesis, and indeed they still do.

The first transition metal alkyls were prepared in 1907, trimethylplatinum compounds being made by Pope and Peachey,[7] while simple gold alkyls were produced by Pope and Gibson.[8]

An upsurge in the study of organotransition metal compounds, however, took place in the early 1950's with the discovery of ferrocene,[9] and the elucidation of its novel "sandwich" structure.[10] Organotransition metal compounds, the study of which had previously been almost totally neglected, were subsequently produced in ever-

increasing numbers, amongst them derivatives of palladium and platinum.

Organoplatinum and -palladium compounds prepared prior to this time had usually contained a platinum-olefin bond. In addition to Zeise's salt, Anderson prepared[11] the dimeric platinum-ethylene compound, $[PtCl_2(C_2H_4)]_2$, in 1934, and the bis(ethylene)platinum compound, $[PtCl_2(C_2H_4)_2]$, was shown[12] to exist at temperatures below $-10^{\circ}C$. The first compounds recognised to contain carbon σ-bonded to platinum or palladium were the alkoxydicyclopentadiene-metal species reported[13,14] by Chatt and coworkers in 1957, though these compounds had been known since about 1900. The first mention of a simple alkylplatinum complex appeared[13] in conjunction with this work, where reference was made to work on the complex $[PtIMe(PPr^n_3)_2]$ by Chatt and Foss. The preparation of a series of alkyl- and arylpalladium complexes was reported[15] in the following year, before Chatt and Shaw published[16] extensive series of platinum alkyls and aryls. Since then organoplatinum and -palladium chemistry has developed rapidly, and has now a very extensive and detailed literature, rivalling those for any other metallic elements.

Organometallic compounds have many synthetic applications, and are now known to be intermediates in a large number of stoichiometric and catalytic reactions.[17] For example, organo-titanium and organoaluminium species are found in the catalytic Ziegler-Natta polymerisation of olefins;[18] organocobalt complexes are implicated in the hydroformylation of olefins (Oxo process);[19] the oxidation of olefins to aldehydes (Wacker process) is catalysed[20] by palladium(II); and Fischer-Tropsch hydrocarbon chain-growth has been shown[21] to take place on a homogeneous tungsten/aluminium catalyst.

Hydrogenation and isomerisation reactions of olefins have been extensively studied using heterogeneous catalysts,[22] whilst in the homogeneous phase olefin isomerisation catalysed by cobalt and iron carbonyl compounds,[23] and the hydrogenation catalyst $[RhCl(PPh_3)_3]$ (Wilkinson's catalyst) have received a lot of attention.[24] Olefin metathesis may also take place as a heterogeneous or a homogeneous reaction.[25] Reactions of acetylenes may also be catalysed by transition metals,[26] their cyclisation to form benzene or cyclooctatetraene being of importance.

The processes involved in homogeneous catalytic systems may closely resemble those which occur heterogeneously at solid surfaces, and recently considerable work has centred on the interface of these two systems, namely the chemistry of cluster compounds. These include closed metal carbonyl clusters, where catalysis may be limited to reactions in which carbon monoxide is involved;[27] one example is the formation of alcohols from olefin, carbon monoxide and water, which is catalysed by derivatives of the $[Fe_3(CO)_{11}H]^-$ anion.[28] Substituted methinyltricobalt clusters were found[29] to catalyse the dimerisation of norbornadiene. Mononuclear ruthenium carbonyl complexes catalyse the hydroformylation of olefins, and a comparative study using $[Ru_3(CO)_{12}]$ showed the cluster compound to be less active.[30]

Thus far the reactions at metal clusters are not well understood, with much effort being expended in their preparation at this stage, rather than in studying their reactions. However, this area of organometallic chemistry, which may be the link between heterogeneous and homogeneous catalyses, is clearly one of considerable importance.

Structure and reactivity.

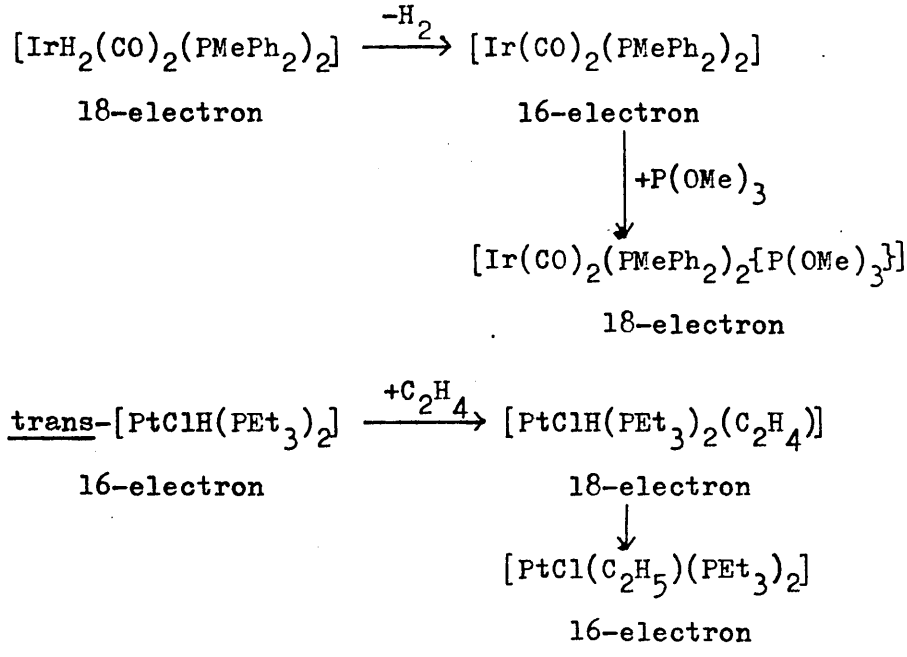
The electron density at the central metal atom is important

as regards stability of transition metal complexes. The so-called "18-electron rule" has long been established,[31] and involves the metal in achieving a formal electron count identical to that of the next higher noble gas. This necessitates filling of the orbitals derived from the one s-, three p- and five d-orbitals of the metal; thus only bonding and non-bonding orbitals are filled, with no electron density being associated with antibonding orbitals, as in the complexes $W(CO)_6$, $Fe(PF_3)_5$ and $Mn(CH_3)(CO)_5$.

As a transition series is traversed in the direction of higher atomic number, however, the increasing nuclear charge results in decreasing energies of the metal d-orbitals. Hence the promotion energies for the nd→(n+1)p electronic transitions increase, and the attainment of the full 18-electron complement becomes less favourable. For the Group VIII metals 16-electron species are common,[32] such as $[PtCl_2(PPh_3)_2]$, while the coinage metals often form 14-electron complexes,[33] such as $[AuMe(PPh_3)]$.

On descending a group it is found that, due to the lanthanide contraction, the nd→(n+1)p promotion energies do not vary regularly.[34] Thus for the nickel triad the energies increase in the order Ni < Pt < Pd, and so for palladium the formation of 18-electron species is least favourable. Similarly rhodium tends to form 16-electron complexes,[35] while iridium commonly forms both 16- and 18-electron species.[36]

A review by Tolman[37] of the 16- and 18-electron rule in organometallic chemistry has been published. This has as its premise that 16- and 18-electron configurations are available to diamagnetic organo-transition metal complexes, and that reactions take place *via* such configurations, other configurations or reaction paths being energetically unfavourable:



Attainment of the 18-electron configuration is dependent on the ligands surrounding the metal centre. Thus the use of multi-electron donors, such as the cyclopentadienyl and arene ligands, is of much importance, especially for the elements of lower atomic number.[38,39] Such ligands are of interest for the Group VIII metals also, and although palladium usually resists addition of ligands beyond the 16-electron configuration stable, 18-electron cyclopentadienylpalladium complexes can be formed.[40]

Since the cyclopentadienyl ligand is formally a five-electron donor, some mention of oxidation state and charge distribution might usefully be made at this point. Although the metal is symmetrically bonded to the cyclopentadienyl ring it is obvious that donation of five units of electronic charge to the metal does not occur. It has recently been shown,[41] by dipole measurements and X-ray photoelectron spectroscopy, that the formal charge on a ligand may be quite different from the value obtained by physical measurement. Thus, for example, the formally unipositive nitrosyl ligand may carry more negative charge than the formally uninegative hydride. By this kind of reasoning there is probably little more

electron density at the metal in the complex $[PdCl(PPh_3)(C_5H_5)]$ - formally an 18-electron species - than in the 16-electron species $[PdCl_2(PPh_3)_2]$. While appreciating these limitations, the concepts of formal oxidation state and 16- and 18-electron species are extremely useful nevertheless, and their applicability to platinum and palladium chemistry will be demonstrated.

Platinum and palladium complexes.

Platinum and palladium commonly form both 16- and 18-electron complexes, with 0, 2 and 4 being the most common oxidation levels. The preference for 16-electron species is more marked in the case of palladium. Thus the chemistry of platinum(IV) is considerably more developed[42] than is that of tetravalent palladium; one example of such is the complex $[PdCl_2(C_6F_5)_2(PPh_3)_2]$, formed by the action of $TlBr(C_6F_5)_2$ on trans-$[PdCl_2(PPh_3)_2]$.[43] Although species of the type PtX_nR_{4-n} are known,[42] all platinum(IV) complexes have octahedral geometry. These are commonly formed by addition of an alkyl halide to the corresponding platinum(II) complex.[44]

The four-coordinate complexes of platinum(II) and palladium(II) have, in nearly every case, square-planar geometry.[45] This is favoured over tetrahedral geometry because, the metal having associated with it eight d-electrons, the high energy $d_{x^2-y^2}$ orbital may be left unoccupied while the four d-orbitals of lower energy are populated.

While the most-studied complexes of platinum and palladium involve the formal oxidation state +2, there is an extensive chemistry of the zerovalent metals. This is largely composed of complexes containing tertiary phosphine ligands,[46] $M(PR_3)_n$ (n = 2, 3 or 4). These may catalyse the oxidation of tertiary phosphine,[47] are implicated in palladium-catalysed vinylic substitution,[48] and can catalyse the water gas shift reaction.[49] Being zerovalent,

these species can perhaps be most realistically compared with the sites involved in heterogeneous catalysis.[50]

A few examples of complexes of platinum and palladium in the +1 oxidation state are known,[51] but those involving the +3 state are rare; they are believed to be produced, for example, as intermediates in the photochemical decomposition of organoplatinum(IV) compounds.[52] The vast majority of the known complexes of platinum and palladium, however, involve the +2 oxidation state of the metal. The preparations of some basic compounds, from which most organoplatinum and -palladium complexes can ultimately be prepared, have been outlined by Hartley.[53] A number of these are dimeric, having bridging halides between the metal centres. These are particularly useful compounds since the bridges may be cleaved, under mild conditions, by a variety of ligands, leading to useful products:[40,45,54-56]

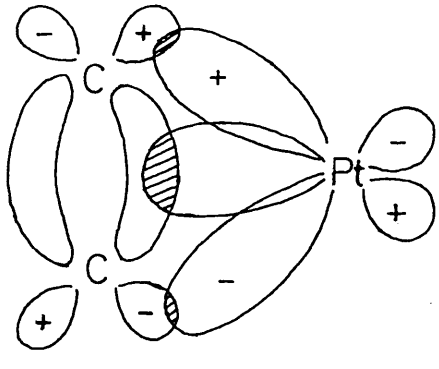
$$[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr^n{}_3)_2] + 2NH_3 \longrightarrow 2\ \underline{trans}\text{-}[PtCl_2(NH_3)(PPr^n{}_3)]$$

Platinum and palladium, especially in their divalent states, form a vast array of organometallic compounds in which a variety of types of metal-carbon bonds are encountered. Metal-alkyls and -aryls involve essentially metal-carbon σ-bonds; the extent of metal-carbon π-bonding in the arylmetal complexes, though small, is uncertain.[57] Calorimetric studies on the reaction of $\underline{trans}$-$[PtPh_2(PEt_3)_2]$ with HCl have led[58] to a minimum energy for the platinum-phenyl σ-bond of 251 kJ mol^{-1}. This is rather less than the energy associated with carbon-carbon or carbon-hydrogen bonds, suggesting that the stability of platinum-carbon σ-bonds is not thermodynamic, but is due to the lack of a suitable decomposition pathway.[45]

Metal-carbonyl and -isocyanide complexes also involve σ-bonds

but, since these ligands are strong π-acceptors, in such compounds the extent of π-donation from the metal to the ligand is considerable. This results in a shortening of the metal-carbon bond in each case[59,60] compared with those found in metal-alkyl complexes.[61] Metal-carbene complexes also exhibit this feature,[62] the unsaturated carbon-metal bond order being greater than unity.

Platinum and palladium also form stable compounds with olefin and acetylene ligands.[63] In such complexes both σ- and π-contributions to the overall bonding are significant. The molecular orbital description of the platinum-olefin bond was proposed by Chatt and Duncanson[64] in 1953, and in essence involves σ-donation from the filled π-orbital of the olefin to the metal, and back-donation from filled orbitals on platinum into the empty π^*-orbital of the olefin. The donation of π-electron density to the metal centre decreases the stretching frequency associated with the carbon-carbon double bond from the value observed for the free olefin, and in $K[PtCl_3(olefin)]$ the stretching frequencies decrease by about 140 cm^{-1} on coordination.[64,65] (Figure 1)



Orbitals used in the combination of ethylene with platinum

Figure 1

A similar, but more marked, decrease in stretching frequency is observed in metal-acetylene complexes,[66-68] the decrease being greater for zerovalent complexes than for those of the divalent metal. In metal-acetylene complexes there are two mutually orthogonal unoccupied π^*-orbitals associated with the acetylene which can overlap suitably orientated filled orbitals of the metal. The metal-acetylene bond is found[69] to be stronger than a corresponding metal-olefin bond, the displacement of ethylene by diphenylacetylene from $[Pt(PPh_3)_2(C_2H_4)]$ occurring with an enthalpy of reaction of -82 ± 12 kJ mol^{-1}. It is also found that the acetylene is considerably distorted from linearity in metal-acetylene complexes,[68,70] indicating some lowering of the carbon-carbon bond order. A distortion of the bond angles in metal-olefin complexes is also observed.

Diolefin-platinum and -palladium complexes may also be formed, and these involve coordination to the metal of two olefinic groups. Such complexes have been prepared using, amongst others, 1,5-cyclooctadiene[71] and norbornadiene.[72] These are particularly useful starting complexes as the diolefin may be readily replaced by a variety of ligands:[71]

$$[Pt(CF_3)_2(cod)] + 2\ PMe_2Ph \longrightarrow [Pt(CF_3)_2(PMe_2Ph)_2]$$

Complexes with three-, four- or five-electron donors are also well established for platinum and palladium. π-Allyl complexes, where the metal cannot be said to be bonded directly to any particular carbon atom of the formal three-electron donor, have been prepared[73] and allylpalladium complexes are involved in a number of organic syntheses.[74] Cyclobutadiene- and cyclopentadienyl-metal complexes, where bonding to the metal is <u>via</u> the delocalised

π-system of the four- or five-membered ring, are also well-known.[40,75-77]

A variation on the theme of platinum and palladium alkyls is the area of metallacycles. In these compounds the metal centre is one component of a ring system. The preparation and thermal decomposition of a series of platinum(II) metallacycles has been investigated by Whitesides,[78,79] and the orbital symmetry restrictions on such thermolyses have recently been outlined.[80] Palladium metallacycles are implicated in a number of stoichiometric and catalytic reactions.[81,82]

A diverse range of reactions are catalysed homogeneously by platinum and palladium systems. These include the dimerisation of ethylene which is accelerated by $[PdCl_2(C_2H_4)]_2$,[83] the oligomerisation of butadiene which is catalysed by bis(cyclooctadiene)-platinum and -palladium,[84] the homogeneous catalysis of olefin hydrogenation by platinum/tin chloride[85] and by ethyleneplatinum[86] systems, and various palladium-catalysed arylation and alkylation reactions.[87]

From this brief summary it is clear that organoplatinum and -palladium chemistry is wide-ranging in its compound types and applications. It is now necessary to gain some insight into the ways in which the ligands determine the geometry, the stability, and the reactivity of the complexes, and the reaction pathways which are available to them.

Reaction pathways of platinum and palladium complexes.

Substitution.

Substitution reactions of square-planar complexes are believed to proceed via a trigonal bipyramidal transition state (Figure 2). Such reactions occur with retention of configuration and it was recognised[88] that certain ligands apparently labilised the bond

trans to themselves. This labilising ability was called "trans-effect", and a series in order of decreasing trans-effect was found to be:[45]

$$C_2H_4 \sim NO \sim CO \sim CN^- > SbR_3 > PR_3 > AsR_3 \sim H^- > CH_3^- > C_6H_5^- > SCN^- > NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$$

Ligands of high trans-effect were those which resulted in the most rapid substitution of the trans-group. The length of the trans-ligand-metal bond was not necessarily affected, however, the

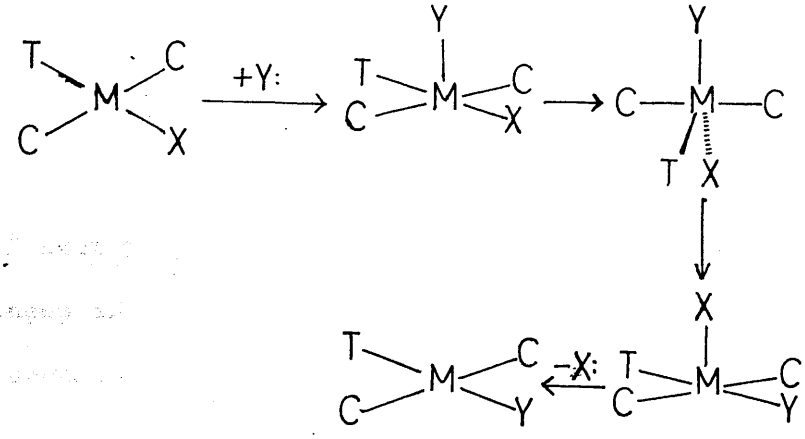


Figure 2

platinum-chlorine bond in Zeise's salt not being significantly lengthened despite the trans ethylene group, while platinum-chlorine bonds trans to hydride are markedly longer than those trans to chloride.

Trans-effect and trans-influence: The trans-effect is now defined as a kinetic phenomenon and for a given ligand T, is related to the rate at which substitution of the trans-ligand X may occur. The overall trans-effect was recognised to involve either σ- or π-bonding contributions, or both.[88] It was realised, for example,

that strong π-accepting groups, such as ethylene or carbon monoxide, would stabilise the five-coordinate transition state by charge removal, particularly in the critical trigonal plane. Thus there is a tendency for the ligands T, X and Y to occupy the trigonal plane, from which X may be expelled. The σ-bond contribution, on the other hand, weakens the bond to the trans-ligand X. This is a thermodynamic phenomenon which can be observed in the ground state, and has been christened "trans-influence". The subject of trans-effects generally has been discussed by Hartley.[89]

The trans-influence of a ligand was first defined as a distinct entity in 1966,[90] and was further discussed by Venanzi[91] in 1968. The whole subject of the measurement and interpretation of the trans-influence was appraised by Clark et al.[92] The original work[90] related to ^{195}Pt-^{31}P nuclear spin coupling constants and it is clear, if such parameters are dominated by the Fermi contact term, that changes in σ-bonding only will be detected, and this would not give an accurate measure of the overall bond strength. Data from X-ray crystallography and vibrational spectroscopy would obviously take account of both σ- and π-bonding contributions, and such measurements have suggested that the latter cannot be ignored when determining trans-influence.[93] An approximate series of ligands in order of decreasing trans-influence, obtained from X-ray structural data, is as follows:[92]

$$R_3Si^- \sim \text{alkyl} \sim H^- \geqslant \text{carbene} \sim PR_3 \geqslant AsR_3 > CO \sim RNC \sim \text{olefin} \sim Cl^- \sim NH_3$$

This may be illustrated by the decreasing platinum-bromine bond length trans to H^- in trans-$[PtBrH(PEt_3)_2]$ (2.56 Å),[94] and trans to Br^- in trans-$[PtBr_2(PEt_3)_2]$ (2.43 Å).[95]

The cis-influence of ligands cannot be overlooked. Calculations

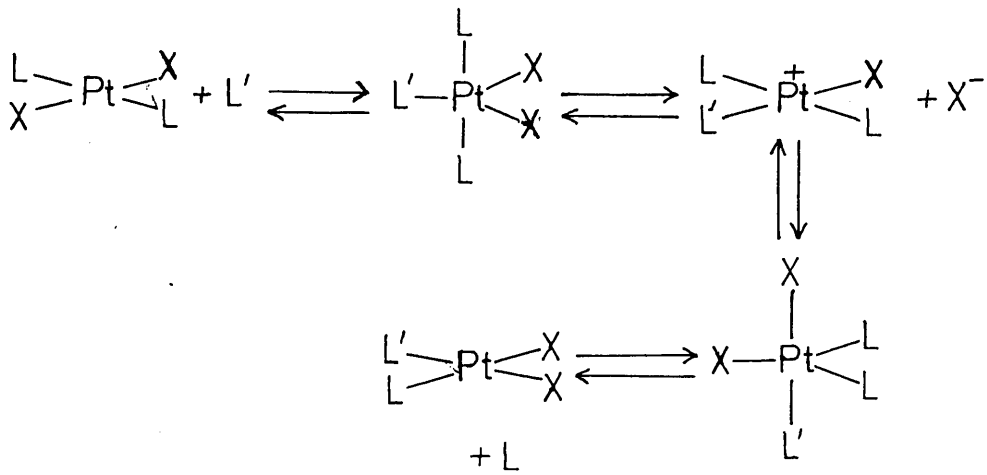
by Zumdahl and Drago[96] suggested that the cis-influence may be only slightly smaller than the trans-influence for any given ligand, but it is generally accepted that the influence of cis-ligands is small by comparison with that of the trans-ligand in square-planar complexes.

It can be seen that this is not a simple area of chemistry, and considerable debate continues over the relative magnitudes of σ- and π-bonding contributions to the trans-influence of a ligand, and the relative importance of cis-ligands.

Isomerisation.

An important consequence of the trans-influence series is the configuration adopted by the ligands about the metal centre; for example, complexes of the type $[PtX_2(PR_3)_2]$ show a preference for cis-geometry, thus avoiding the situation where two groups of high trans-influence occupy mutually trans positions. If a situation arises, therefore, where the thermodynamically more stable isomer is not that which is initially formed, isomerisation can occur. For square-planar complexes of platinum, isomerisation is generally slow except when a catalyst, such as a free nucleophile, is present.

Such isomerisations were commonly believed to occur by a double displacement sequence, involving trigonal bipyramidal intermediates:[97]



Other mechanisms have been postulated, however, including pseudo-rotation of a five-coordinate intermediate,[98] and various solvent-assisted processes.[99,100] The possibility of a dissociative mechanism, involving "cis-like" and "trans-like" T-shaped intermediates, was suggested[101] for the uncatalysed cis-trans isomerisation of complexes of the type $[PtXR(PEt_3)_2]$. The possible implication of such reactive intermediates, and the role of solvent-assisted pathways, have been highlighted in recent reviews.[102,103] Isomerisation can also be effected by the action of heat or by photochemical means; for example, heating cis-$[PtCl(C_6F_5)(PEt_3)_2]$ to 230°C at 0.6 torr resulted in conversion to the trans-isomer.[104]

Thus it is apparent that the subject of isomerisation of square-planar complexes is not straightforward, and it is likely that several reaction pathways are possible.

Oxidative addition.

The oxidative addition reaction effectively involves insertion of a metal centre into an element-element bond, the end result being an increase by two in both the coordination number and formal oxidation state of the metal:

$$L_xM^{n+} + A-B \longrightarrow L_xM\begin{matrix}A\\B\end{matrix}^{(n+2)+}$$

A number of reviews of this type of reaction have been published, including those undergone by complexes of platinum and palladium.[44,46] Both zero- and divalent metal complexes undergo oxidative addition, the former usually following partial dissociation:[105]

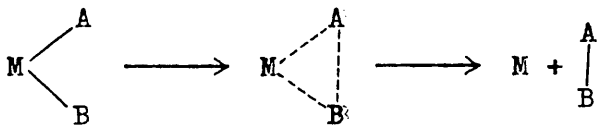
$$[Pt(PPh_3)_4] \xrightarrow{-2PPh_3} [Pt(PPh_3)_2] \xrightarrow{+RX} [PtXR(PPh_3)_2]$$

Platinum(IV) complexes can readily be formed by oxidative addition of the divalent metal species.[42] Such reactions may involve the addition of halogen,[16,106] alkyl halide,[16,107] or insertion of the metal centre into germanium-, tin- or lead-halide bonds.[108]

The mechanism of oxidative addition of organic halide is uncertain with three possible routes having been advanced;[44] an S_N2 attack on carbon by the metal, a concerted attack of the metal on the carbon-halide bond to give a three-centre intermediate, or a radical process. The mechanism seems to depend on both the transition metal and the organic halide.[44] Oxidative addition reactions often result in trans-products, although a concerted trans-addition is symmetry forbidden. The addition of HX to trans-$[Pt(CN)H(PEt_3)_2]$ at low temperature, however, gave cis- and trans-products,[109] suggesting that concerted cis-addition may be one operative mechanism, although a two-stage ionic reaction sequence may also be involved.

Reductive elimination.

In many respects reductive elimination is the reverse of the oxidative addition reaction, with the formal oxidation state and coordination number each being decreased by two units. In general, combination of the two eliminated groups via a chemical bond is involved in a concerted process:



Such reactions are more common for transition metals in their higher oxidation states, and may involve, for example, elimination of hydrogen,[110] hydrogen chloride,[111] or ethane.[112] That reductive elimination is a concerted process was shown[113] for the elimination

of ethane from $[PtIMe_3(PMe_2Ph)_2]$.

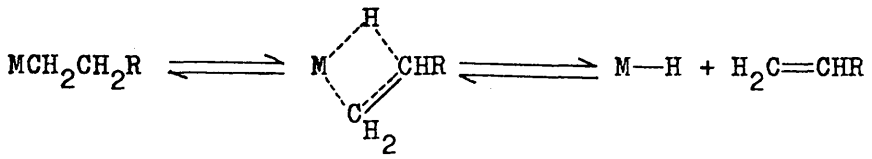
Although oxidative insertion of a metal centre into a carbon-carbon bond is uncommon, reductive elimination with the concomitant formation of a carbon-carbon bond is well-known.[79,112-114] In fact, oxidative addition of alkyl halide followed by reductive elimination of two alkyl groups is fairly common and effectively results in displacement of the organic group by halide; for example, addition of iodomethane to methylgold(I) complexes results in the formation of ethane:[115]

$$[Au(CH_3)(PMe_3)] + CH_3I \longrightarrow [AuI(PMe_3)] + C_2H_6$$

Consecutive oxidative addition/reductive elimination processes are fairly widespread. Other examples include the addition of HCl to $[PtClH(PEt_3)_2]$ and subsequent elimination of hydrogen to form $[PtCl_2(PEt_3)_2]$,[116] and the action of iodomethane on $[Au(CH_2SiMe_3)(PPh_3)]$ followed by reductive elimination of $Si(Et)Me_3$.[115] In fact it has been suggested[117] that, in general, cleavage of alkyl- or arylplatinum bonds by electrophiles occurs by an oxidative addition/reductive elimination sequence.

<u>β-Elimination.</u>

Unlike the preceding reactions, β-elimination generally involves no overall change of coordination number or formal oxidation state. It is believed to be a concerted reaction, and the main requirement is a substituent on the β-carbon which may become bonded directly to the metal, generally a hydrogen atom, and a vacant coordination site on the metal.[118] The process, which involves a σ-π rearrangement may be represented as depicted below:



The mechanism was shown[119] to involve transfer of a hydrogen atom from the β-carbon atom to the metal using the partially deuteriated copper complex $[Cu(CH_2CD_2CH_2CH_3)(PBu_3)]$.

The simplest β-elimination is that in which ethylene is lost from an ethylmetal complex. Such an example was reported in 1962, when it was shown that pyrolysis of an ethylplatinum compound led to ethylene production:[120]

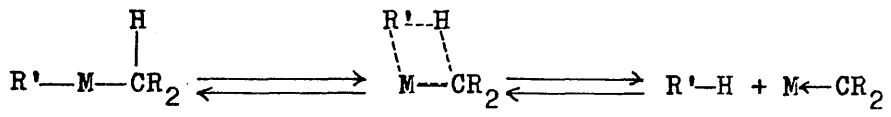
$$\underline{trans}\text{-}[PtClEt(PEt_3)_2] \longrightarrow \underline{trans}\text{-}[PtClH(PEt_3)_2] + C_2H_4$$

The reaction was found to be revesible, however, and treatment of the hydridoplatinum complex at high ethylene pressures caused formation of some ethylplatinum complex.

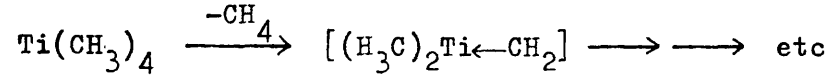
The ease with which such reactions may take place is such that, to avoid complications due to competitive β-elimination reactions, it is often necessary to use organic groups which do not possess this facility, such as the methyl, benzyl and trimethylsilylmethyl groups.

α-Elimination.

This process involves elimination of two fragments originally bonded to the metal and the α-carbon atom, the latter commonly being hydrogen. The mechanism may involve hydride transfer to the metal followed by reductive elimination, or a concerted process:



Thermolysis of tetramethyltitanium has been shown,[121] by deuterium labelling experiments, to proceed by α-hydride elimination, titanium carbide being the final product:

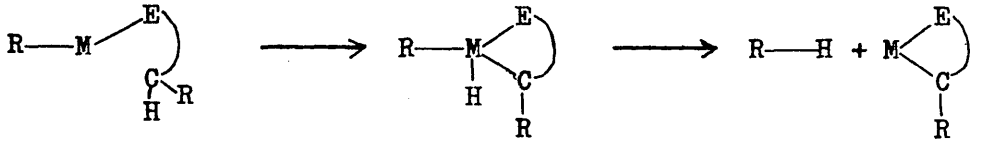


The reversible reaction of $[W(C_5H_5)_2Me(PR_3)]^+$ to form $[W(C_5H_5)_2H(CH_2PR_3)]^+$ is formulated[122] as proceeding <u>via</u> α-transfer of hydride to form a methylenetungsten species. Recently a mechanism for stereospecific olefin polymerisation by Ziegler-Natta catalysts has been suggested[123] which involves α-transfer of hydride to the titanium centre. Such reversible α-hydrogen transfer processes may be important in many such reactions, with or without the associated elimination step.

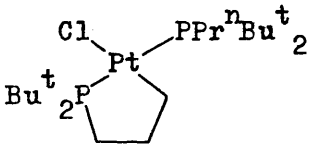
Finally it should be noted that α- and β-eliminations may also be called (1,2)- and (1,3)-eliminations respectively, and as such form part of a whole series of (1,n)-elimination reactions of which they are, perhaps, the best documented members.

<u>Internal metallation.</u>

Internal metallations, which are examples of (1,n)-eliminations, involve the formation of a bond between a transition metal and a carbon atom within a coordinated ligand. This almost invariably involves insertion of the metal into a carbon-hydrogen bond with or without subsequent reductive elimination:



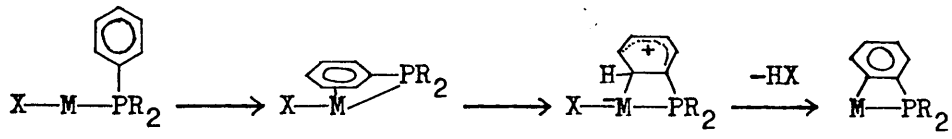
In $[PtCl_2(PPr^nBu^t_2)_2]$ internal metallation of the γ-carbon atom of the n-propyl group, followed by reductive elimination of HCl results in formation of complex A.[124]



(A)

The most widely documented form of internal metallation is that of ortho-metallation of coordinated arylphosphines.[125] Examples include the ortho-metallations of triphenylphosphine in $[IrCl(PPh_3)_3]$ with the formation of a hydridoiridium(III) complex,[126] and in $[RhMe(PPh_3)_3]$ to produce methane and no change in the formal oxidation state of the metal.[127]

Despite the large number of examples of ortho-metallation the mechanism of the process is not fully known. From studies on substituted azobenzene complexes it appears that the aromatic ring undergoes electrophilic substitution by the metal.[128] Thus initial formation of a metal-arene π-complex followed by electrophilic attack on the aromatic ring would lead, after reductive elimination, to the observed product:[125]



In cases where an increase in oxidation state occurs the final step of HX elimination would not take place.

The size of the ring formed during internal metallation is clearly of some import. It has been shown[129] that the preference is to form five-membered rings rather than six- or four-membered ones, from H/D exchange reactions of alkylphosphineplatinum complexes. Deuterium incorporation was found mainly at the C-3 position of n-propyl- and n-butylphosphines, this being an example of a reversible internal metallation reaction.

Binuclear elimination.

This is a reductive elimination process in which two metal atoms have both their coordination numbers and oxidation states reduced by one. Elimination of a species formed from two fragments, each originally bound to a different metal centre, occurs with simultaneous metal-metal bond or metal-alkyl bridge formation. Such an elimination process is implicated in the production of ethane from $AuMe(PPh_3)$,[112] and in the thermolysis of $Ag(n\text{-}C_4H_9)(PBu^n_3)$ to yield n-octane.[130]

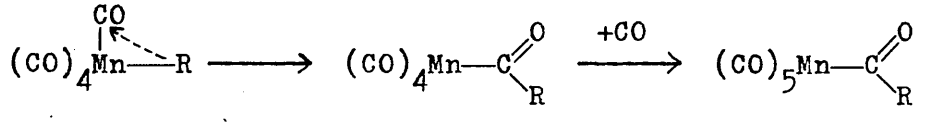
Insertion reactions.

In transition metal chemistry an insertion reaction may be defined as the insertion of a molecular fragment, previously in the coordination sphere of the metal, into an element-metal bond. Insertions into metal-hydrogen, metal-carbon, metal-halide and metal-metal bonds are known, but only the more common reactions involving metal-carbon and metal-hydrogen bonds will be covered here.

Comprehensive reviews of insertion reactions in general are quite abundant.[131-134] More specific articles are available on the insertion of carbon monoxide,[135-137] sulphur dioxide,[138]

isonitriles,[139] and olefins[140] and acetylenes.[141]

The insertion of carbon monoxide into a metal-carbon bond was first observed[142] for alkyl(pentacarbonyl)manganese systems in 1957. The kinetics were shown from isotopic labelling studies to be consistent with an alkyl migration mechanism,[143] whereby the alkyl group migrates to and becomes bonded to a coordinated CO ligand before nucleophilic attack on the metal by another CO molecule:



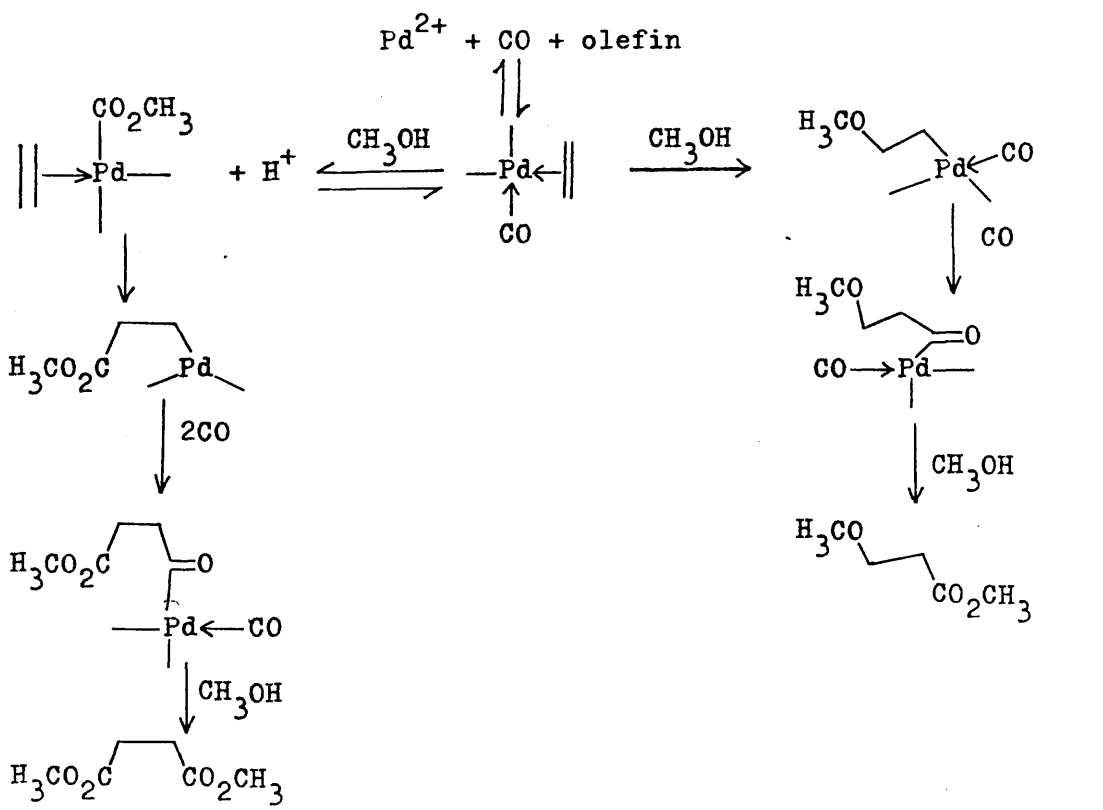
Formation of acylmetal derivatives from initially uncoordinated carbon monoxide was achieved by Booth and Chatt,[144] who found that treatment of alkylplatinum and -palladium complexes with carbon monoxide in solution resulted in the isolation of the corresponding acylmetal complexes.

The "alkyl migration" or "carbonyl insertion" reaction has been the subject of a recent molecular orbital study,[145] and this particular insertion reaction will be considered in much greater detail in a later section.

The insertions of acetylenes and olefins into metal-hydrogen bonds are well established, and of considerable interest because such processes are believed to be implicated in olefin and acetylene polymerisations and other catalytic reactions. The insertion of an olefin into a metal-hydrogen bond is, in fact, the reverse of the β-elimination reaction. The olefin insertion reaction has recently been investigated on a theoretical basis,[146] and has been the subject of a number of kinetic studies.[147-150] The mechanism is still a matter of debate, however, with solvent-assisted, associative and dissociative pathways having been postulated.

Acetylene insertion into metal-hydrogen bonds to produce vinyl-metal complexes is also well-known, but again the mechanism has not been thoroughly elucidated. Mechanisms involving insertion from four-coordinate[151] and five-coordinate[152] intermediates have been proposed, and free radicals have been detected[153] in the reaction of trans-$[PtClH(PEt_3)_2]$ with acetylene. The reactions are significantly affected by the electron-withdrawing or -donating abilities of the substituents in substituted acetylenes and olefins.[151] It is worth noting, however, that no unambiguous example involving a straightforward insertion of an acetylene or olefin into a metal-carbon bond has been reported.[123]

Insertion steps are believed to be involved in a number of reactions catalysed by transition metal complexes, including acetylene trimerisation[26] and olefin hydrogenation.[24] A catalytic cycle has been developed[154] for the olefin carbonylation reaction using palladium(II) chloride in methanol, the reaction scheme suggested involving insertion of both carbon monoxide and olefin:

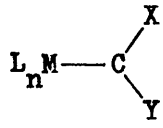


CHAPTER TWO

Carbene Complexes of Platinum

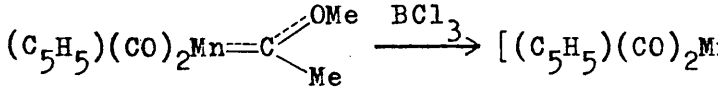
Introduction.

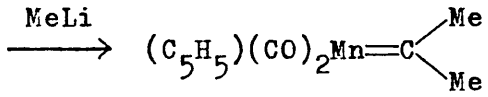
Metal-carbene complexes are of the general form shown below:



The first complexes of this type were prepared by Chugaev in 1915,[155] although they were not recognised as such until recently,[156] but within the last twenty years the growth of this area of organometallic chemistry has been the subject of a number of reviews,[157-161] while others have concentrated on the intermediacy of such species in catalytic and stoichiometric reactions,[162] and it is now recognised that carbene intermediates may be involved in many processes including olefin metathesis and cyclopropanation.[162,163] The use of transition metal carbene complexes in organic synthesis has also been explored.[164]

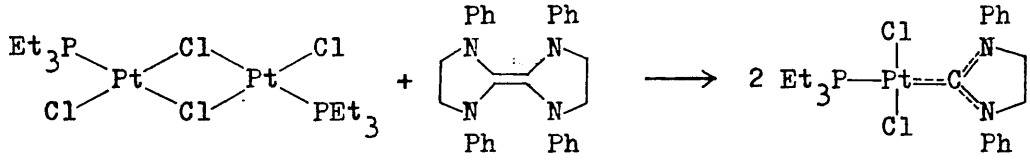
This area of organometallic chemistry was further extended in 1973 when Fischer prepared the first metal carbyne complexes.[165] Such species have since been prepared for several transition elements,[161] and may be found as isolable intermediates during the modification of carbene moieties:[166]





Although such species are as yet unknown for platinum and palladium, these metals have extensive carbene chemistries.

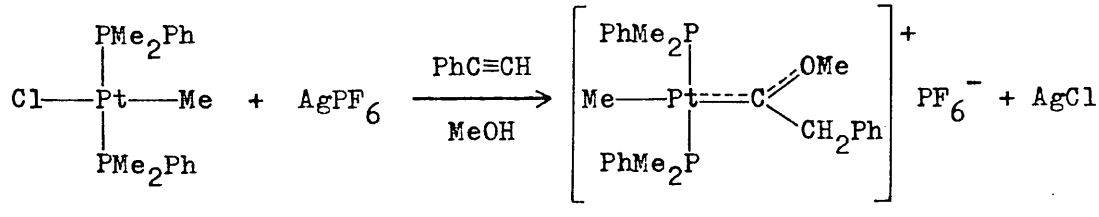
Carbene complexes have been prepared with platinum in its +2 and +4 oxidation states, and with various groups bonded to the carbene carbon atom. Cleavage of an electron-rich olefin in the presence of a halide-bridged platinum dimer results in the formation of neutral carbene complexes with the carbene carbon atom attached to two nitrogen atoms:[167]



Treatment of platinum-isocyanide complexes with alcohols results in the formation of alkoxy(amino)carbene complexes:[168]

$$\underline{cis}\text{-}[PtCl_2(CNPh)(PEt_3)] \xrightarrow[reflux]{EtOH} \underline{cis}\text{-}[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$$

Cationic alkoxy(alkyl)carbene complexes may be obtained by treating $\underline{trans}$-$[PtXR(PR'_3)_2]$ with a silver salt in alcoholic solvent in the presence of a monosubstituted acetylene:[169]



Platinum(IV) carbene complexes have been prepared both by oxidative addition of chlorine to carbene complexes of the divalent metal,[170] and by carbene formation at a tetravalent site,[171] but are rare in comparison to their platinum(II) analogues nevertheless. Addition of methylamine to the tetrakis(methylisocyanide)platinum cation resulted in formation of the first example of a platinum centre solely coordinated by carbene ligands:[172]

$$[Pt(CNMe)_4]^{2+}\ (PF_6^-)_2 + 4\ MeNH_2 \longrightarrow [Pt\{C(NHMe)_2\}_4]^{2+}\ (PF_6^-)_2$$

Although transition metal carbene complexes contain a formal metal-carbon double bond, this is not truly reflected in the metal-carbon bond distance. A brief series of platinum-carbon bond lengths, each with a trans platinum-chlorine bond, for various carbon ligands is given in Table 1.

complex	Pt-C distance (Å)	reference
trans-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$	2.079	173
cis-$[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$	1.96(2)	174
cis-$[PtCl_2\{C(NPhCH_2)_2\}(PEt_3)]$	2.009	175
cis-$[PtCl_2(CNPh)(PEt_2Ph)]$	1.83(4)	176
cis-$[PtCl_2(CO)(PEt_3)]$	1.855	177

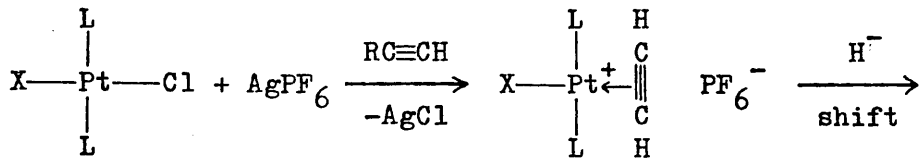
Table 1

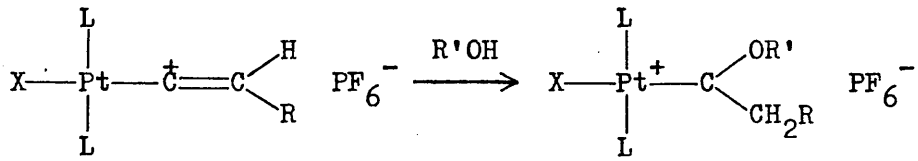
Comparison of the platinum-carbon bond lengths of the carbene complexes with that in the platinum-alkyl complex, trans-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$, shows that some degree of multiple bonding does exist. A further shortening of the metal-carbon distance is observed, however, in the isocyanide and carbonyl complexes, suggesting that in these species there is a greater degree of multiple bonding. Thus isocyanide and carbonyl ligands are better π-acceptors than carbenes,[176] the double bond formalism for metal-carbene bonding thus having only minor physical significance. The degree of unsaturation which does exist, however, may lead to interesting properties and reactions.

Results and discussion.

The only alkoxy(organo)carbene complexes of platinum previously prepared, either by the reaction of acetylenes and alcohols with platinum halide complexes[169] or by the action of alcohols on the metal acetylides or α-chlorovinyls,[178] have been cationic in nature.

It was proposed that formation of such complexes proceeded via a platinum-stabilised carbonium ion:[179]

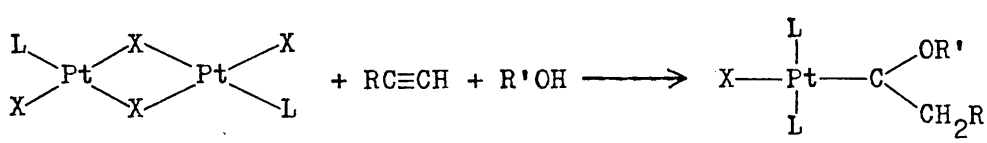




The use of non-coordinating anions, such as PF_6^-, was necessary in order to prevent nucleophilic attack at the coordinated carbene ligand, leading to decomposition. The effect of the positive charge on the ease of formation and stability of these compounds was of interest, so it was decided to prepare a corresponding series of electroneutral complexes and investigate their properties and reactivities.

Preparation of electroneutral platinum-carbene complexes.

Treatment at room temperature of chloroform solutions of the dimeric, halide-bridged platinum complexes, $[Pt_2(\mu\text{-}X)_2X_2L_2]$ (X = Cl, Br or I; L = PMe_2Ph or PEt_3), with monosubstituted acetylenes, RC≡CH (R = Me, Et or Ph), and alcohols, R'OH (R' = Me, Et or Pr^n), led to the formation of electroneutral alkoxy(organo)carbene derivatives:



Reactions with acetylene itself (R = H) were unsuccessful, presumably owing to competing side reactions.[179]

The complexes are colourless, crystalline solids which are stable to air and moisture. They are soluble in chloroform and methylene chloride, but are only sparingly so in benzene, acetone or methanol. Thus preparations in methanolic solvent led to lower yields, possibly due to the relatively insoluble nature of both reactant and product complexes. Preparations in chloroform solution led to yields of between 30% and 70%, being greatest in the cases where X = Br. The bromide complexes also appear the most resistant to thermal decomposition, while the chloride complexes decompose to the extent of ca 20% over 24 hours at 60°C. Chloroform solutions of all the complexes, however, survive for several days at ambient temperature with little decomposition.

The reaction rates and yields were generally increased if at least a 50% excess of the acetylene was employed. This suggests that the first step of the reaction is formation, by halide bridge cleavage, of a platinum-acetylene complex:

$$[Pt_2(\mu\text{-}X)_2X_2L_2] + 2\ RC{\equiv}CH \rightleftharpoons 2[PtX_2L(RC{\equiv}CH)]$$

Alkoxycarbene formation could then result from rearrangement to a vinylidene intermediate, as proposed by Chisholm and Clark,[179] followed by attack of the alcohol. If this route is followed then vinylidene intermediates must exist in neutral form also, which possibility has been suggested.[178] Thus it is apparent that a positive charge is not necessary either for the formation of platinum(II) alkoxy(organo)carbene complexes from acetylenes and alcohols, or for their subsequent stabilisation.

Spectroscopic studies of the complexes.

That the products had a cis-configuration was apparent from the far infrared spectra of the chloride complexes, and from the

^{31}P n.m.r. spectra of all the complexes. Each of the chlorides showed two ν(Pt-Cl) stretching frequencies at ca 310 and 290 cm^{-1}, the two bands being of equal intensity. Two such bands are expected for cis-dichloroplatinum complexes,[112] and the values obtained are similar to those reported for other cis-dichloro(carbene)platinum(II) species.[168]

Further evidence for cis-geometry was obtained from the ^{31}P n.m.r. spectra of the complexes. They all show $^{1}J(^{195}Pt-^{31}P)$ coupling constants around 3600 Hz, which are similar to those found in cis-$[PtX_2(PR_3)_2]$ complexes.[180,181] The coupling constants closely resemble that for cis-$[PtCl_2(PEt_3)_2]$,[180] while those in cis-$[PtCl_2(CO)(PEt_3)]$[177] and cis-$[PtCl_2(CNPh)(PEt_3)]$[181] are reduced to 2754 Hz and 3049 Hz respectively. Also, the ν(Pt-Cl) stretching frequencies are similar to those in cis-$[PtCl_2(PEt_3)_2]$ (305 and 283 cm^{-1}),[112] and from these two observations it appears that the alkoxy(organo)carbene ligands have a trans-influence similar to those of tertiary phosphines. Such a claim has already been made for alkoxy(amino)carbene ligands,[168,175] and this point will be pursued in the following section. It may also be noted that the ^{1}J(Pt-P) coupling constants are dependent on the halide present, decreasing in the order Cl > Br > I. This may reflect their trans-influences, a similar trend having been observed in the complexes cis-$[PtX_2(PBu_3)_2]$ (X = Cl, Br or I).[90] The ir. and ^{31}P n.m.r. data are given, with other characterisation data, in Table 2.

The ^{1}H n.m.r. spectra reveal a number of interesting features, and these data are presented in Table 3. The benzyl methylene groups of the alkoxy(benzyl)carbene complexes give rise to AB patterns, and the phosphine methyl groups of the dimethylphenylphosphine complexes are non-equivalent (Figure 3). Both of these features are indicative of hindered rotation about the platinum-carbene carbon

Characterisation data for the complexes cis-$[PtX_2\{C(OR)R'\}L]$

					Found			Calculated				
X	L	R	R'	m.pt.(°C)	C	H	X	C	H	X	ν(Pt-Cl)/cm^{-1}	^1J(Pt-P)/Hz
Cl	PMe_2Ph	Me	CH_2Ph	118-119	37.84	3.90	13.77	37.92	3.93	13.18	312, 289	3754
Cl	PMe_2Ph	Et	CH_2Ph	124-125	39.24	4.24	12.88	39.13	4.20	12.84	317, 288	3764
Cl	PMe_2Ph	Pr^n	CH_2Ph	144-145	40.09	4.32		40.29	4.45		312, 287	
Cl	PMe_2Ph	Me	Et	122-123	30.50	3.97	15.30	30.25	4.02	14.89	312, 289	3763
Cl	PMe_2Ph	Et	Et	139-141	32.19	4.46		31.84	4.32		311, 288	
Cl	PMe_2Ph	Et	Pr^n	128-129	33.39	4.63	13.81	33.33	4.60	14.07	313, 283	3778
Cl	PEt_3	Me	CH_2Ph	122-123	34.55	4.73		34.75	4.86		312, 285	3690
Cl	PEt_3	Et	Pr^n	150-151	29.83	5.32		29.75	5.62		311, 286	3726
Br	PMe_2Ph	Me	CH_2Ph	126-127	32.41	3.27	25.54	32.54	3.38	25.49		3723
Br	PMe_2Ph	Et	CH_2Ph	137-138	33.74	3.59	24.84	33.70	3.62	24.93		3733
Br	PMe_2Ph	Me	Et	126-127	25.56	3.26	28.22	25.49	3.39	28.28		
Br	PMe_2Ph	Et	Et	130-131	27.17	3.64	27.44	26.94	3.66	27.60		
Br	PEt_3	Me	CH_2Ph	124-125	29.61	3.73		29.65	4.15			
I	PMe_2Ph	Me	CH_2Ph	121-122	27.99	2.69		28.22	2.93			3589
I	PMe_2Ph	Me	Et	120-121	21.50	2.79	38.79	21.79	2.90	38.70		3596
I	PEt_3	Me	CH_2Ph	116	25.49	3.61	35.99	25.68	3.59	36.23		

Table 2

Proton n.m.r. data for the complexes cis-$[PtX_2\{C(OR)CH_2R'\}L]$ - Table 3

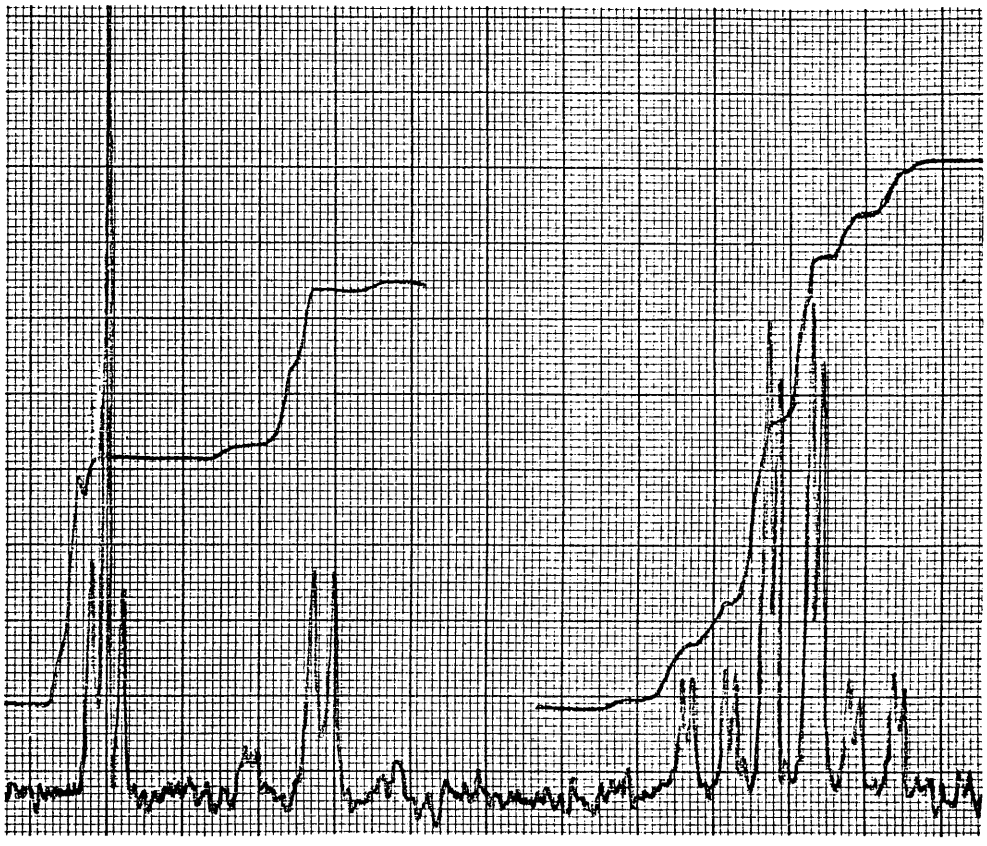
				phosphine methyls			α-alkoxy protons			α-carbene protons		
X	L	R	R'	$(CH_3)^a$	^2J(P-H)	^3J(Pt-H)	(OCH_2-)	^4J(Pt-H)	$^3J(CH_2-CH_2-)$	(CH_2R')	^2J(H-H')	$^3J(CH_2-CH_2-)$
Cl	PMe_2Ph	Me	Ph	1.80	11.5	45.0	4.92	8.2		4.11	17.7	
				1.76						3.73		
Cl	PMe_2Ph	Et	Ph[c]	1.78	11.7	44.6	5.73	8.6	7.2	4.11	17.6	
				1.73			5.11			3.77		
Cl	PMe_2Ph	Pr^n	Ph	1.77	11.5	46.0	5.53	d	d	4.09	18.0	
				1.73			4.91			3.72		
Cl	PMe_2Ph	Me	Me	2.07	11.7	44.8	4.92	8.2		2.64		7.0
				2.00								
Cl	PMe_2Ph	Et	Me	2.05	11.7	45.0	d	d	7.2	2.75		7.0
				1.97								
Cl	PMe_2Ph	Et	Et	2.05	12.0	44.2	5.67	d	7.0	2.62		d
				1.96			5.10					
Cl	PEt_3	Me	Ph				4.95	8.2		4.35	18.0	
										4.00		
Cl	PEt_3	Et	Et[c]				5.89	d	7.2	d		7.0
							5.30					
Br	PMe_2Ph	Me	Ph	1.86	12.0	46.0	4.88	8.5		4.29	17.8	
				1.84						3.81		

Proton n.m.r. data for the complexes cis-$[PtX_2\{C(OR)CH_2R'\}L]$ - Table 3 (cont'd)

				phosphine methyls			α-alkoxy protons			α-carbene protons		
X	L	R	R'	$(\underline{CH}_3)^a$	$^2J(P-H)^b$	$^3J(Pt-H)$	$(O\underline{CH}_2-)$	$^4J(Pt-H)$	$^3J(CH_2-CH_2-)$	$(\underline{CH}_2R')$	$^2J(H-H')$	$^3J(CH_2-CH_2-)$
Br	PMe_2Ph	Et	Ph	1.83	11.5	47.0	d	d	7.0	4.25	17.8	
				1.79						3.83		
Br	PMe_2Ph	Me	Me	2.15	11.5	46.0	4.88	8.2		2.70		7.0
				2.09								
Br	PMe_2Ph	Et	Me	2.12	11.5	46.0	d	d	7.0	2.70		7.0
				2.05								
Br	PEt_3	Me	Ph				4.83	8.5		4.47	18.0	
										4.07		
I	PMe_2Ph	Me	Ph	1.92	11.5	45.5	4.71	8.5		4.54	18.5	
										3.97		
I	PMe_2Ph	Me	Me	2.19	11.5	44.5	4.72	8.0		2.83		7.0
				2.12								
I	PEt_3	Me	Ph				4.73	e		4.78	18.0	
										4.29		

(a) chemical shifts measured in p.p.m. downfield of TMS (b) coupling constants measured in Hz (c) -alkoxy protons, $^2J(H-H')$ 10.5 Hz (d) unresolved (e) unresolved due to overlap of the $-CH_2-$ signal

bond, and the inherent asymmetry thus produced. In some cases the non-equivalence of the phosphine methyl groups could be removed by changing the solvent, this presumably being due to coincidental chemical shifts of these groups. The $^{2}J(P-H)$ and $^{3}J(Pt-H)$ coupling



^{1}H n.m.r. spectrum of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$

Figure 3

constants of 11.5 Hz and 45 Hz respectively are typical for PMe_2Ph trans to halide.[182]

The $-OCH_2-$ hydrogens of the ethoxy- and propoxycarbene complexes also exhibit non-equivalence. In each compound, a chemical shift difference of ca 0.6 p.p.m. is observed (Table 3), suggesting that, on average, they occupy very different magnetic environments.

Long-range coupling of platinum-195 to the alkoxy groups is present in all cases, but can only be clearly resolved in the methoxycarbene complexes. As shown in Figure 3, they give rise to

a 1:4:1 triplet (^4J(Pt-H) ca 8 Hz). Irradiation of the ethyl $-CH_3$ groups in cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$ and cis-$[PtCl_2\{C(OEt)Pr^n\}(PEt_3)]$ results in each of the $-OCH_2CH_3$ signals collapsing to a broadened doublet (due to ^2J(H-H')), but ^4J(Pt-H) is not fully resolved. Similarly the α-carbene carbon hydrogen signals of the benzyl, ethyl and propyl groups are broadened by coupling to platinum, but ^3J(Pt-H) values have not been obtained.

The various examples of non-equivalence led to an interest in determining the solid state structure of one of the complexes, in order to investigate whether these features persist within the crystalline material.

X-ray structural determination of cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$.

The crystal structure was determined by X-ray diffraction methods by Drs. Lj. Manojlović-Muir and K. W. Muir, and R. A. Wales, in this department. The molecules were found to have a square-planar configuration, the out-of-plane distortions in the coordination sphere of platinum being negligible (Figure 4). The platinum-carbon bond length of 1.920(9) Å is shorter than the values of 1.96(2) and 2.009 Å for the complexes cis-$[PtCl_2(PEt_3)L]$, where L is C(OEt)-NHPh[174] and $C(NPhCH_2)_2$[175] respectively. Such variations probably reflect small changes in the extent of Pt→C back-bonding, giving rise to a π-acidity series of the carbene ligands:

$$C(OEt)CH_2Ph > C(OEt)NHPh > C(NPhCH_2)_2$$

It has been suggested[93] that increasing π-acidity should lead to a lower trans-influence. The platinum-chlorine bond distance trans to the carbene ligand is 2.375(3) Å, longer than those trans to C(OEt)NHPh[174] and $C(NPhCH_2)_2$[175] (2.361(5) and 2.362(3) Å respectively). This apparent conflict may be due to perturbation of

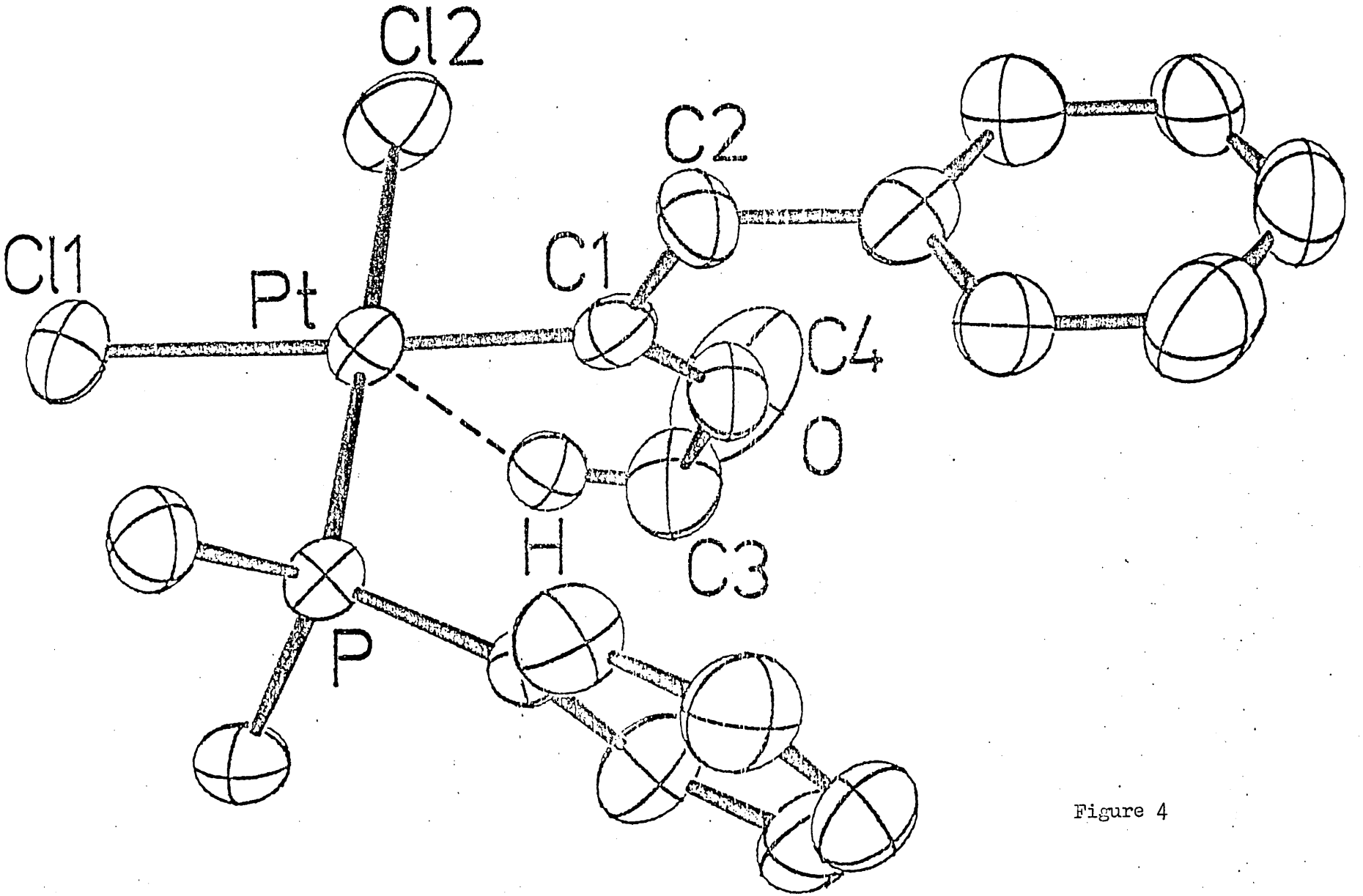


Figure 4

the bond length in cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$ by a short, intramolecular Pt---H contact (see below), which is not observed in the other complexes. The Pt-Cl bond length trans to PMe_2Ph is 2.355(3) Å, suggesting that the PMe_2Ph and $C(OEt)CH_2Ph$ ligands exert similar trans-influences on Pt-Cl bonds.

The orientation of the carbene ligand about the platinum-carbon bond is such that it makes a dihedral angle of 85° with the platinum coordination plane. Values of 70-90° have been found for other platinum-carbene complexes.[174,175] An interesting feature of the structure is a short, intramolecular Pt---H contact of 2.59(8) Å (Figure 4). Although shorter metal-hydrogen contacts are known (for example, distances of ca 2.0 Å were found in two molybdenum pyrazolylborate complexes[183]), a metal-hydrogen contact of 2.8 Å in $[RhCl(PPh_3)_3]$ has been considered to be of structural and chemical significance.[184] It has been suggested that such contacts represent "non-primary valence interactions", formally providing the metal with a noble gas configuration.

These latter two features of the molecular structure may account for the unusual aspects of the ^1H n.m.r. spectrum of cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$. If the plane of the carbene ligand remains perpendicular to the coordination plane of platinum in solution, as might be prescribed for steric reasons, then the non-equivalence of the phosphine methyl groups and of the benzyl methylene hydrogens would result. The intramolecular Pt---H contact would cause the two hydrogens of the $-OCH_2-$ group to occupy very different environments, and it would appear from the ^1H n.m.r. spectrum that this phenomenon persists in solution, at ambient temperature at least. Moreover, it seems likely that such a Pt---H interaction may be a general feature of this series of complexes.

Reactions of platinum carbene complexes.

A number of reactions are undergone by the electroneutral carbene complexes which bear interesting comparison with those of the analogous cationic derivatives.

When cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ was treated with CD_3OD, exchange of the benzyl $-CH_2-$ hydrogens for deuterium resulted. Monitoring the reaction by ^1H n.m.r. spectroscopy showed the exchange to be complete within five minutes at room temperature.

Similar reactions were found for cationic alkoxy(organo)carbene complexes, the H/D exchange being complete after one hour:[178]

$$\text{trans-}[PtX\{C(OMe)CH_2R\}L_2]^+ \xrightarrow[1h]{R'OD} \text{trans-}[PtX\{C(OMe)CD_2R\}L_2]^+$$

A slower reaction with alcohols resulted in alkoxy group exchange, this process requiring about 12 hours for completion:[178]

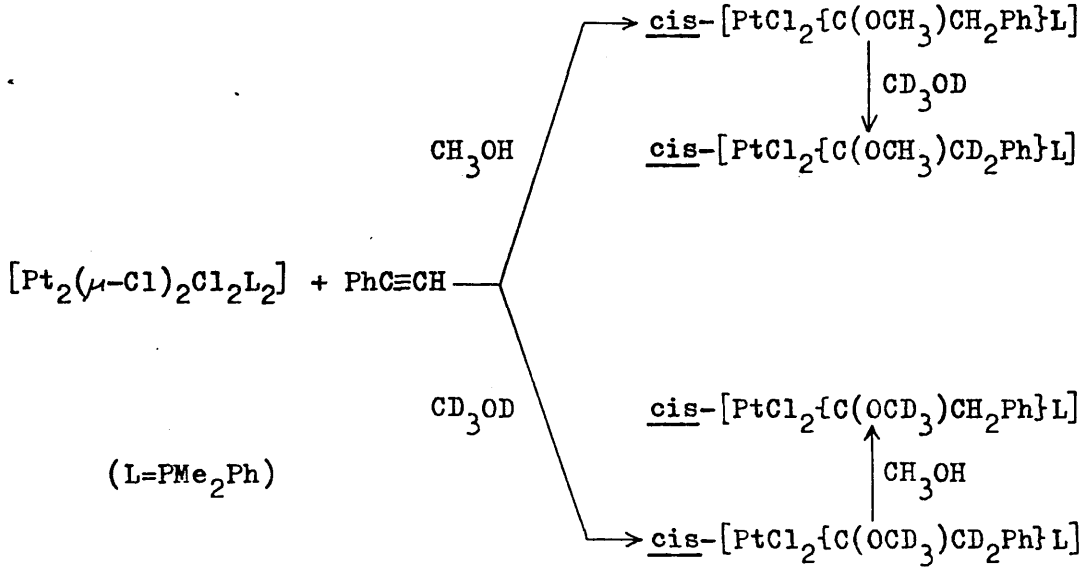
$$\text{trans-}[PtX\{C(OMe)CH_2R\}L_2]^+ \xrightarrow[12h]{R'OH} \text{trans-}[PtX\{C(OR')CH_2R\}L_2]^+$$

It was suggested that the H/D exchange proceeds *via* reversible removal of H^+ to form an α-methoxyvinylplatinum intermediate, whilst alkoxy group exchange is the result of nucleophilic attack of the entering alcohol at the carbene carbon atom. The rates of both processes seemed likely to be enhanced by the overall positive charge on the complex, and indeed both reactions were slowed when chloride was replaced by ligands of poorer electron-withdrawing ability.[178]

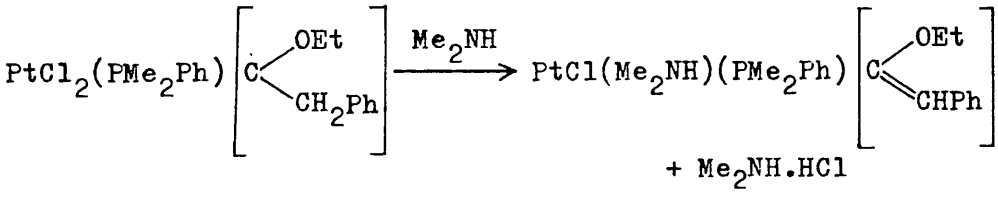
Treatment of the electroneutral complexes with CD_3OD failed to produce any visible signs of alkoxy group exchange after 24 hours, and after 72 hours slight decomposition made analysis of the ^1H n.m.r. spectrum more difficult. Similarly treatment of ethoxy-

(organo)carbene complexes with methanol, or methoxy(organo)carbene complexes with ethanol, failed to show any signs of exchange after 24 hours at ambient temperature. This slow rate of alkoxy group exchange is understandable in terms of the loss of the overall positive charge, but it is clear that the rate of H/D exchange may not be explained so simply.

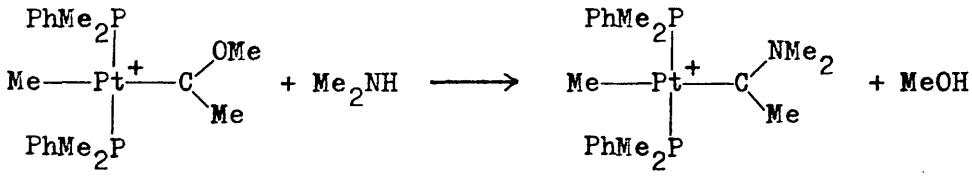
The relative rates of these two processes for the electroneutral complexes meant that a variety of partially deuteriated complexes could be prepared by suitable use of deuteriated alcohols:



The rapid H/D exchange reaction of the neutral complexes suggests an enhanced acidity of the α-carbene hydrogens. Despite the lack of an overall positive charge it is unlikely that a different mechanism is operative, since treatment of cis-[$PtCl_2$-{C(OEt)CH_2Ph}(PMe_2Ph)] with dimethylamine leads to proton abstraction and formation of an ethoxyvinylplatinum complex:



It was unclear from ir. and n.m.r. spectra, however, which geometry the ethoxyvinylplatinum complex adopted. This reaction further emphasises the reaction rate differences between the neutral and cationic alkoxy(organo)carbene complexes. When treated with secondary amines the cationic complexes readily liberate alcohol to produce amino(organo)carbene complexes:[185]



The corresponding chloroplatinum complexes, however, reacted to produce the acylplatinum complex and a quaternary ammonium salt:[185]

$$\underline{\text{trans}}\text{-}[PtCl\{C(OMe)Me\}(PMe_2Ph)]^+ + Me_2NH \longrightarrow$$

$$\underline{\text{trans}}\text{-}[PtCl(COMe)(PMe_2Ph)_2] + Me_3NH^+$$

Only when treated with tertiary amines, where the possibility of amino(organo)carbene complex formation was not available, did the cationic complexes produce alkoxyvinylplatinum complexes.[178] In the neutral case, halide abstraction also occurs, the vacant coordination site becoming occupied by a further dimethylamine molecule.

The mechanism of H/D exchange of the α-carbene hydrogens may indeed be one of alkoxyvinylplatinum formation, but it is not clear whether this occurs by direct proton abstraction, or whether nucleophilic attack on or hydrogen transfer to the metal centre might also be involved. Nevertheless, it is certain that these reactions cannot simply be explained in terms of the presence or absence of an overall positive charge on the complex.

Finally, an alternative view of the relationship between the cationic and neutral carbene complexes is that they are related by

a change of one ligand cis to the carbene moiety. When one tertiary phosphine ligand in trans-$[PtCl\{C(OMe)CH_2Ph\}(PMe_2Ph)_2]^+$ is replaced by chloride the neutral complex, cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$, results. It is thus apparent that the above reactions of the carbene ligand are affected by a change of cis-ligand as well as by replacement of that in the trans-position.[178] Moreover, the rates of H/D exchange of the α-carbene hydrogens and alkoxy group exchange are apparently affected in opposite directions by a change of cis-ligand, whereas trans-ligand variations affect the rates in a similar way.[178]

When chloroform solutions of the neutral chloride carbene complexes were heated to 60°C they decomposed slowly (ca 20% after 24 hours). When cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ was heated at 60°C for five days the production of methyl chloride was evident in the ^1H n.m.r. spectrum (a sharp singlet at δ3.0), the carbene -OMe signal diminishing simultaneously, and the solution ir. spectrum showed an intense band at 1654 cm^{-1} as well as several weaker bands in the 2000-2200 cm^{-1} region. Reaction to produce an acylplatinum complex as the major product was apparently taking place:

$$2\ \text{cis-}[PtCl_2\{C(OMe)Et\}(PMe_2Ph)] \longrightarrow [Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2] + 2\ MeCl$$

Evidence for the nature of the product was gained by preparing the chloride-bridged acylplatinum complex by reaction of cis-$[PtCl_2(CO)(PMe_2Ph)]$ with $HgEt_2$.[186] The product was isolated as a colourless, crystalline material, and in chloroform solution produced a strong ν(CO) band at 1654 cm^{-1}. On allowing the carbene solution to stand at ambient temperature for a further several weeks the presence of cis-$[PtCl_2(CO)(PMe_2Ph)]$ and cis-$[PtCl_2(PMe_2Ph)_2]$ were detected by

^{31}P n.m.r. spectroscopy (^{1}J(Pt-P) 2850 Hz and 3550 Hz respectively), by comparison with spectra recorded for authentic samples. These compounds were also detected in a chloroform solution of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ which had been allowed to stand for a similar period.

This tendency towards secondary decomposition was more pronounced with the alkoxy(benzyl)carbene complexes. Under similar conditions, methyl chloride elimination from cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$, and ethyl chloride production in the case of cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$, could be monitored by ^{1}H n.m.r. spectroscopy. Thus it appears that decomposition by alkyl halide elimination is a general process for these complexes. In alkoxy(benzyl)carbene complex decomposition, however, no acyl derivatives were detected. Instead a variety of infrared absorptions between 2000 and 2200 cm^{-1} were observed, suggesting the formation of complexes containing terminal carbonyl ligands, and again cis-$[PtCl_2(CO)(PMe_2Ph)]$ and cis-$[PtCl_2(PMe_2Ph)_2]$ were eventually produced amongst other, unidentified decomposition products. An identical product mixture resulted from the reaction of cis-$[PtCl_2(CO)(PMe_2Ph)]$ with $Hg(CH_2Ph)_2$, however, suggesting that the complications arose from secondary processes rather than from an alternative decomposition pathway of the carbene complexes.

The above decomposition is catalysed by the addition of ionic halide. When cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ in methylene chloride was treated with tetraethylammonium chloride at room temperature, the ^{1}H n.m.r. spectrum after 18 hours showed total loss of the carbene -OMe signal at δ4.92 and 100% production of methyl chloride. The ir. spectrum revealed the presence in solution of the usual variety of decomposition products. Addition of tetraethylammonium trifluoromethanesulphonate to cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$

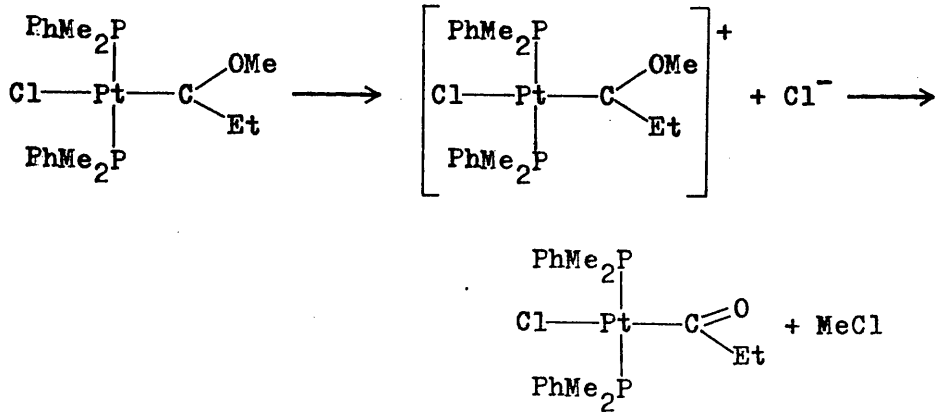
caused no reaction. After five days the ^1H n.m.r. spectrum corresponded exactly to a mixture of starting materials.

The catalysed decomposition is likely to proceed *via* nucleophilic attack by the halide. Thus, while *cis*-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ readily methylates chloride ions, no reaction is observed with the less nucleophilic $SO_3CF_3^-$ anion. Ionic halides cause similar reactions with cationic carbene complexes, methyl chloride slowly being eliminated when *trans*-$[PtMe\{C(OMe)Me\}(PMe_2Ph)_2]^+ PF_6^-$ was treated with HCl, and *trans*-$[PtCl(COMe)(PMe_2Ph)_2]$ being the only isolable platinum-containing product.[185]

A similar effect was observed when a neutral carbene complex was treated with tertiary phosphine. Addition to a chloroform solution of *cis*-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ of one molar equivalent of dimethylphenylphosphine showed, in the ^1H n.m.r. spectrum after 24 hours, total loss of the carbene -OMe signal, a strong singlet at $\delta 3.0$ due to methyl chloride and a triplet pattern, with ^{195}Pt satellites, for the phosphine methyls. The latter is indicative of two phosphines in mutually *trans* positions.[106a] From this reaction was obtained the acylbis(dimethylphenylphosphine)platinum complex:

$$\textit{cis}\text{-}[PtCl_2\{C(OMe)Et\}(PMe_2Ph)] + PMe_2Ph \longrightarrow \textit{trans}\text{-}[PtCl(COEt)(PMe_2Ph)_2] + MeCl$$

The reaction is likely to proceed by two distinct steps, initial displacement of chloride by tertiary phosphine being followed by nucleophilic attack of chloride ion, resulting in methyl chloride elimination:



In agreement with this sequence, when the reaction was carried out in the presence of silver trifluoromethanesulphonate, to remove the chloride ion from solution, the cationic carbene complex was isolated almost quantitatively as its $SO_3CF_3^-$ salt:

$$\underline{cis}\text{-}[PtCl_2\{C(OMe)Et\}(PMe_2Ph)] + PMe_2Ph \xrightarrow{AgSO_3CF_3}$$

$$\underline{trans}\text{-}[PtCl\{C(OMe)Et\}(PMe_2Ph)_2]^+ SO_3CF_3^- + AgCl$$

The cationic ethoxy(ethyl)carbene complex was also isolated in this manner. These complexes are of the type prepared by Chisholm and Clark.[169] They can also be conveniently synthesised by treating acylbis(tertiary phosphine)platinum complexes with methylating agents such as methyl trifluoromethanesulphonate. Thus the acyl-platinum complexes produced by reaction of the neutral complexes with tertiary phosphine may be readily converted into the corresponding cationic carbene complexes by such treatment. One such preparation had previously been carried out using $MeSO_3CF_3$.[178]

This method has one major advantage over the acetylene/alcohol route, since the use of aroylplatinum species leads to cationic alkoxy(aryl)carbeneplatinum complexes, which had not previously

been prepared. One such example was therefore isolated:

$$\underline{\text{trans}}\text{-}[PtCl(COPh)(PEt_3)_2] + MeSO_3CF_3 \longrightarrow$$

$$\underline{\text{trans}}\text{-}[PtCl\{C(OMe)Ph\}(PEt_3)_2]^+ SO_3CF_3^-$$

Reactions with $MeSO_3F$ and $Me_3O^+ PF_6^-$ were also attempted, but the rates and yields of reaction were poorer than when $MeSO_3CF_3$ was employed. All three methylating agents failed to react with the halide-bridged aroylplatinum complex, $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PEt_3)_2]$, so cationic, dimeric carbene species could not be produced by this route.

Treatment of the electroneutral carbene complexes with $AgSO_3CF_3$, $MeSO_3CF_3$, or $EtSO_3CF_3$ resulted in halide removal, as evidenced by AgCl precipitation or the ^1H n.m.r. signals expected for MeCl or EtCl. The identity of the platinum-containing product is proposed to be a dimeric, halide-bridged, cationic carbene complex:

$$2\ \underline{\text{cis}}\text{-}[PtCl_2\{C(OMe)Et\}(PMe_2Ph)] + 2\ MeSO_3CF_3 \longrightarrow$$

$$[Pt_2(\mu\text{-}Cl)_2\{C(OMe)Et\}_2(PMe_2Ph)_2]^{2+} (SO_3CF_3^-)_2 + 2\ MeCl$$

In no case was it possible to isolate the dimeric carbene complexes so formed, however, as they steadily react further, finally producing mixtures of acyl- and/or carbonylplatinum species similar to those which result from the thermal decomposition of the neutral complexes. There is considerable evidence for such complexes being produced, however:

(1) The reactions could be followed by ^1H n.m.r. spectroscopy by

observing the growth of a new methoxy signal (with ^{195}Pt satellites) at δ5.1, and the simultaneous production of AgCl, MeCl or EtCl.

(2) When cis-$[PtBr_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ was treated with $AgSO_3CF_3$ the ^{31}P n.m.r. spectrum at -60°C showed a number of signals, all having $^1J(Pt-P)$ coupling constants in the region of 3800 Hz (although at room temperature only one broad signal with ^{195}Pt satellites was observed). It seems probable that only dimeric species, where cis and trans-isomers and various orientations of the two carbene ligands are possible, could account for this large number of signals. On warming to room temperature the complexes decomposed within two hours to give a mixture of unidentified products.

(3) Halide abstraction from other cis-dihaloplatinum complexes by $MeSO_3F$ is known to produce related halide-bridged dimers:[187]

$$2\text{cis-}[PtBr_2(PEt_3)_2] + 2MeSO_3F \longrightarrow [Pt_2(\mu\text{-}Br)_2(PEt_3)_4]^{2+}(SO_3F^-)_2 + 2MeBr$$

(4) It was possible to carry out bridge-splitting reactions on solutions of the complexes before decomposition had progressed significantly. Addition of tetraethylammonium chloride caused the methoxy signal in the ^1H n.m.r. spectrum to return to its original position, suggesting that regeneration of the electroneutral carbene complex had occurred. The introduction of tertiary phosphine to a solution containing $[Pt_2(\mu\text{-}Cl)_2\{C(OMe)Et\}_2(PMe_2Ph)_2]^{2+}$ $(SO_3CF_3^-)_2$ resulted in the formation of the known complex trans-$[PtCl\{C(OMe)Et\}(PMe_2Ph)_2]^+$ $SO_3CF_3^-$.

Although the isolation of these dimeric carbene complexes did not prove feasible, the evidence for their existence therefore appears convincing. Thus, treatment of cis-$[PtCl_2\{C(OEt)Pr^n\}(PEt_3)]$

with $MeSO_3CF_3$ caused liberation of methyl chloride and the production of the corresponding dimeric carbene complex. On standing for four days at ambient temperature $EtSO_3CF_3$ was observed, by ^1H n.m.r. spectroscopy, in the reaction mixture. In a similar experiment addition of $EtSO_3CF_3$ to a solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ caused the liberation of ethyl chloride and, after six days, the presence of $MeSO_3CF_3$ was detected. The ir. spectrum of this solution exhibited a strong band at 1654 cm^{-1}, due to the chloride-bridged acylplatinum dimer. It appears, therefore, that these cationic, dimeric carbene complexes are extremely powerful alkylating agents, capable of alkylating even the non-nucleophilic $SO_3CF_3^-$ anion:

$$[Pt_2(\mu\text{-}Cl)_2\{C(OMe)Et\}_2(PMe_2Ph)_2]^{2+} + 2\ SO_3CF_3^- \xrightarrow{6\ days}$$

$$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2] + 2\ MeSO_3CF_3$$

This observation accounts for the inaccessibility of cationic, dimeric carbene complexes by alkylation of the corresponding halide-bridged acylplatinum dimers, since the equilibrium position lies well to the side of the acyl complexes:

$$[Pt_2Cl_2(COR)_2L_2] + 2\ MeSO_3CF_3 \rightleftharpoons [Pt_2Cl_2\{C(OMe)R\}_2L_2]^{2+}\ (SO_3CF_3^-)_2$$

This means that dimeric alkoxy(aryl)carbene compounds cannot be prepared; hence a route to electroneutral species by halide addition is also unavailable.

Since these cationic, halide-bridged carbene complexes alkylate the $SO_3CF_3^-$ anion, attempts were made to isolate them as their PF_6^- or SbF_6^- salts. Treatment of the neutral complex, cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$, with $AgPF_6$ or $(Me_3O)PF_6$, however,

did not result in the isolation of the dimeric complex. Instead, the normally unreactive PF_6^- anion[188] degraded to PF_5 (and POF_3 and SiF_4, presumably from traces of moisture and glass), possibly by methyl fluoride elimination, although this was not detected. The familiar mixture of acyl and terminal carbonyl compounds was evident from the solutionir. spectrum. The only identifiable product from the reaction with $AgSbF_6$ was $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, the fate of the methyl group remaining unknown.

The reason for the powerful alkylating ability of the dimeric carbene complexes is not understood. Both the neutral and cationic monomeric alkoxy(organo)carbeneplatinum complexes readily alkylate halide ions, but neither shows any tendency to react similarly towards the less nucleophilic $SO_3CF_3^-$ anion.

It was found that treatment of the neutral carbene complexes with Lewis acids, as in the reaction with Ag^+, produced an intractable mixture containing various acyl and carbonyl products. Thus addition of BCl_3 to a solution of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ caused broadening of the -OMe signal in the ^1H n.m.r. spectrum, and the solutionir. spectrum showed several absorptions in the 2000-2200 cm^{-1} region. The similarity of this result to that obtained on addition of Ag^+ suggests that BCl_3 reacts with the complex by halide abstraction to produce the BCl_4^- salt of the cationic, dimeric carbene complex. This may be contrasted with the work of Fischer, who found that the action of BCl_3 on alkoxy(alkyl)-carbene complexes of chromium, molybdenum and tungsten resulted in formation of metal-carbyne complexes:[165]

$$(CO)_5M{-}C(OMe)(Me) + BCl_3 \longrightarrow Cl(CO)_4M{\equiv}CMe + \{BCl_2(OMe)\}$$

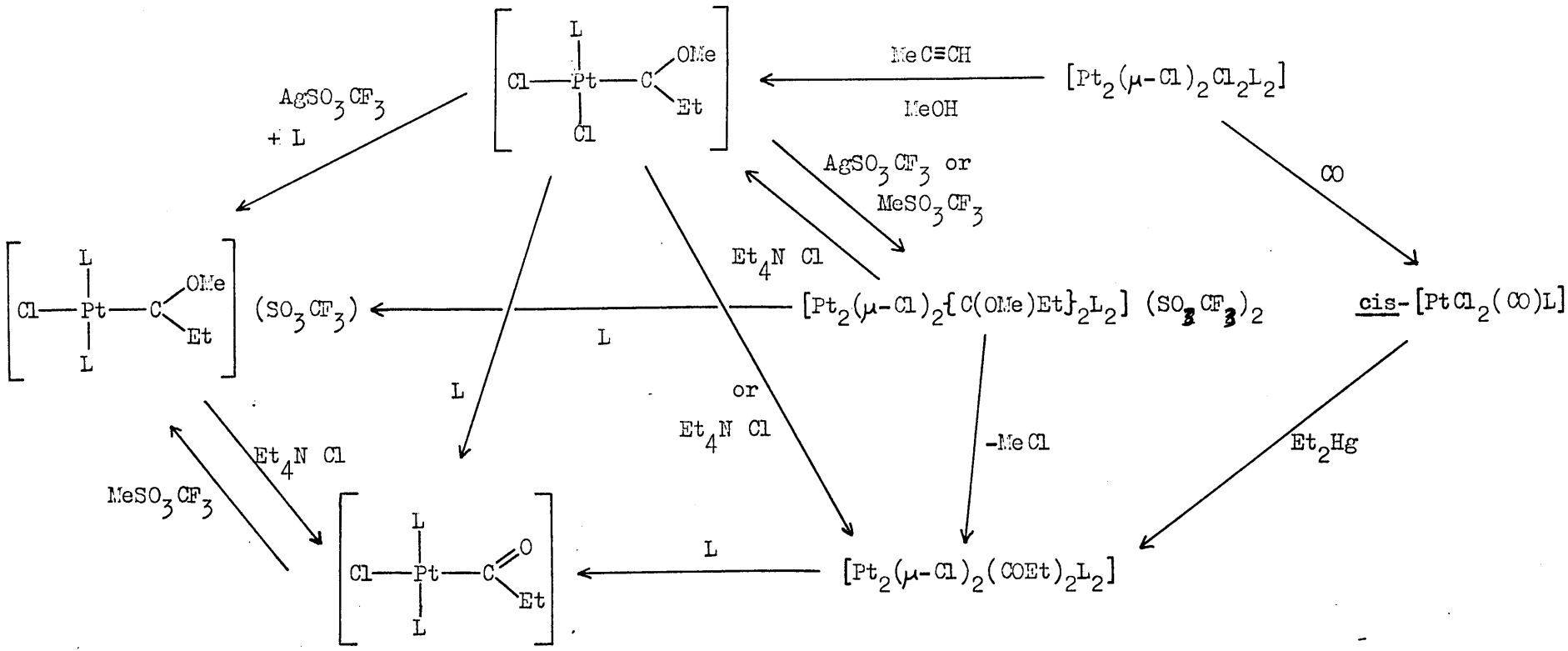
In those cases the possibility of halide abstraction was not available, however, the supporting ligands being carbon monoxide only.

When the cationic complex trans-$[PtCl\{C(OMe)Ph\}(PEt_3)_2]^+$ $SO_3CF_3^-$ was treated with $AgPF_6$, BCl_3 or other Lewis acids no isolable products emerged. Broadening of the -OMe signal was again evident in the ^1H n.m.r. spectrum, and eventually terminal carbonyl bands were observed in the ir. spectrum. Reactions with $AlCl_3$, $SiCl_4$ or $SnCl_4$ were unsuccessful, being considerably slower than those with BCl_3. Again it appears that BCl_3 reacts by halide abstraction, since the product mixture closely resembled that obtained by reaction with $AgPF_6$. Thus it appears that, while halides are present as supporting ligands, reaction pathways which involve halide abstraction are favoured over those which involve attack at the coordinated carbene ligand.

Conclusions.

A number of interesting points have emerged from the preparation and reactions of the electroneutral carbene complexes. Firstly, the acetylene/alcohol route to alkoxy(organo)carbene complexes is not limited to positively-charged complexes. Since dimeric species $[Pt_2(\mu\text{-}X)_2X_2(PR_3)_2]$ react to produce neutral dihalo-alkoxy(organo)carbene complexes, the possibility of synthesising derivatives from halide-bridged dimers of the type $[Pt_2(\mu\text{-}X)_2R'_2(PR_3)_2]$ (R' = Ph, acyl or aroyl) is evident. The effect of the organic group on the reactions of such complexes would be of considerable interest.

The reactions of the carbene ligand - in particular the rates of H/D and alkoxy group exchange - are clearly not simply dependent on the overall charge on the complex. Although the rates of H/D exchange in the cationic complexes, trans-$[PtX\{C(OMe)Me\}(PMe_2Ph)_2]^+$


MeC≡CH
MeOH
$[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$
$AgSO_3CF_3$ + L
$AgSO_3CF_3$ or $MeSO_3CF_3$
CO
Et_4N Cl
(SO_3CF_3)
$[Pt_2(\mu\text{-}Cl)_2\{C(OMe)Et\}_2L_2]$ $(SO_3CF_3)_2$
cis-$[PtCl_2(CO)L]$
L
L
or
Et_4N Cl
-MeCl
Et_2Hg
Et_4N Cl
$MeSO_3CF_3$
L
$[Pt_2(\mu\text{-}Cl)_2(COEt)_2L_2]$
(L = PMe_2Ph or PEt_3)

Scheme 1

PF_6^-, appear to reflect the electron-withdrawing ability of the ligand X,[178] the relative rates of the two exchange processes for the neutral complexes suggest that other factors may be involved. Again, the strong alkylating ability of the halide-bridged, dimeric, cationic carbene complexes seems unlikely to be due merely to their overall charge, since the monomeric, cationic complexes do not share this property.

The decomposition of the neutral carbene complexes involves alkyl halide elimination. The complexity of the final product mixture seems to arise from secondary decompositions involving acyl- and carbonylplatinum species. The relationships between the carbene and acyl complexes are depicted in Scheme 1.

Experimental.

Infrared spectra of solid products as KBr discs were recorded on Perkin Elmer 225 and 580 spectrophotometers. Infrared spectra of reaction mixtures in $CDCl_3$ solution were recorded on a Perkin Elmer 577 instrument (ca 0.08 M solutions in 0.5 mm NaCl solution cells). ^1H N.m.r. spectra were recorded in $CDCl_3$ solution using a Varian T-60 spectrometer, ^{31}P and ^{19}F n.m.r. spectra being obtained from a Varian XL-100 spectrometer. Microanalyses (C, H and N) were performed on a Perkin Elmer 240 analyser; for compounds containing deuterium the sensitivity factor was corrected for the anticipated H:D ratio.

All the neutral carbene complexes were prepared by similar procedures. A typical example is given.

cis-Dibromo(ethoxybenzylcarbene)dimethylphenylphosphineplatinum: $[Pt_2(\mu\text{-}Br)_2Br_2(PMe_2Ph)_2]$ (0.630g, 0.639 mmol) was dissolved in chloroform ($50cm^3$) under nitrogen and ethanol ($4cm^3$) was added. Phenylacetylene ($0.20cm^3$, 1.79 mmol) was introduced and the solution was stirred at ambient temperature for 8 h. The solvent was then

removed to leave a light brown solid which was dried *in vacuo* to remove traces of phenylacetylene. This solid was stirred vigourously in benzene and filtered to remove brown, soluble, organic materials. The nearly white solid was crystallised from methylene chloride/diethyl ether, giving fine, white crystals of *cis*-$[PtBr_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$ (0.459g, 56%).

In those preparations where methyl- or ethylacetylene was used, the gas was passed through a chloroform solution of the dimeric platinum complex to which the desired alcohol had been added.

Preparation of partially deuteriated carbene complexes.

To a pure chloroform solution ($35cm^3$) of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ (0.561g, 0.695 mmol) was added phenylacetylene ($0.20cm^3$, 1.79 mmol) and d_4-methanol ($1.0cm^3$). The solution was stirred for 18 h, after which time the solvent was removed. After treatment with benzene to remove soluble, organic materials, the residue was crystallised from CH_2Cl_2/Et_2O to yield colourless crystals of *cis*-$[PtCl_2\{C(OCD_3)CD_2Ph\}(PMe_2Ph)]$, m.pt. 127-128°C. (Found: C 37.66, H+D 4.67, Cl 13.50% Required for $C_{17}H_{16}Cl_2D_5OPPt$: C 37.57, H+D 4.83, Cl 13.06%)

Treatment of this complex in chloroform solution with CH_3OH for *ca* 1 h, followed by crystallisation of the residue from CH_2Cl_2/Et_2O, gave *cis*-$[PtCl_2\{C(OCD_3)CH_2Ph\}(PMe_2Ph)]$, m.pt. 121-122°C. (Found: C 37.56, H+D 4.32, Cl 13.40% Required for $C_{17}H_{18}Cl_2D_3OPPt$: C 37.71, H+D 4.47, Cl 13.11%)

Similarly, treatment of the fully hydrogenated version with CD_3OD gave *cis*-$[PtCl_2\{C(OCH_3)CD_2Ph\}(PMe_2Ph)]$, m.pt. 124-125°C. (Found: C 37.93, H+D 4.36, Cl 13.00% Required for $C_{17}H_{19}Cl_2D_2OPPt$: C 37.78, H+D 4.29, Cl 13.13%)

Reaction of cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$ with Me_2NH.

To a solution of cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$ (0.138g, 0.250 mmol) in chloroform ($15cm^3$) was added excess Me_2NH. The solution was stirred for 2 h, the solvent was removed, and the oily residue was pumped to remove unreacted amine. Treatment with benzene produced a small amount of greyish solid, which was identified as $Me_2NH.HCl$ by comparison of its ir. spectrum with that of a genuine sample. Addition of n-pentane to the benzene solution precipitated a white solid, which was recrystallised from Et_2O to give white crystals of $[PtCl\{C(OEt)=CHPh\}(Me_2NH)(PMe_2Ph)]$, m.pt. 175-176°C. (Found: C 43.18, H 5.32, N 2.47% Calculated for $C_{20}H_{29}ClNOPPt$: C 42.82, H 5.22, N 2.50%)

Di-μ-chlorodipropionylbis(dimethylphenylphosphine)diplatinum: cis-$[PtCl_2(CO)(PMe_2Ph)]$ (1.29g, 2.98 mmol) was suspended in benzene ($50cm^3$) and diethylmercury ($0.32cm^3$, 3.01 mmol) was added. After 1 h the black solution was filtered, the solvent was removed, and the residue was pumped to remove traces of unreacted $HgEt_2$. Ethylmercuric chloride was removed by sublimation at 55°C/0.001 torr for 48 h. The remaining solid was recrystallised from benzene/pentane, then from CH_2Cl_2/Et_2O to yield colourless crystals of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, m.pt. 136-138°C ($\nu$(CO) 1654 cm^{-1}). (Found: C 31.18, H 3.75, Cl 8.80% Calculated for $C_{22}H_{32}Cl_2O_2P_2Pt_2$: C 31.02, H 3.79, Cl 8.34%)

Decomposition of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$.

A solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (33.4mg) in $CDCl_3$ ($2.5cm^3$) was heated to 60°C in air for 5 days. The solution ir. spectrum then showed the existence of an intense band at 1654 cm^{-1}, due to $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, and several weaker bands in the 2000-2200 cm^{-1} region. The ^1H n.m.r. spectrum showed a complex pattern in the phosphine methyl region, and the absence of a methoxy

signal at δ4.92 from the starting material.

After further standing at room temperature for 55 days the ^{31}P n.m.r. spectrum showed the presence of cis-$[PtCl_2(CO)(PMe_2Ph)]$ and cis-$[PtCl_2(PMe_2Ph)_2]$ (^1J(Pt-P) 2850 Hz and 3550 Hz respectively) amongst other products. The ir. spectrum no longer showed the presence of the acyl complex, but exhibited several strong bands in the 2000-2200 cm^{-1} region.

When cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ or cis-$[PtCl_2\{C(OEt)CH_2Ph\}(PMe_2Ph)]$ was treated in the same manner no acyl complex was detected in the solution ir. spectrum, but several bands in the 2000-2200 cm^{-1} region were observed.

Reaction of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ with $Et_4N^+ Cl^-$.

To a solution of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ (32.4mg, 0.060 mmol) in methylene chloride ($3cm^3$) was added $Et_4N^+ Cl^-.H_2O$ (11.3mg, 0.062 mmol). The solution was stirred for 18 h and the ^1H n.m.r. spectrum showed the presence of MeCl (sharp singlet at δ3.0). The solvent was removed and the residue was dissolved in $CDCl_3$. The total loss of the -OMe signal at δ4.92 showed that the reaction had gone to completion. The solution ir. spectrum showed several absorptions in the 2000-2200 cm^{-1} region, identical to those present after thermolysis of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$.

Treatment of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ with $Et_4N^+ SO_3CF_3^-$.

To a solution of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ (20.0mg, 0.037 mmol) in $CDCl_3$ was added $Et_4N^+ SO_3CF_3^-$ (2.7mg, 0.010 mmol). After 5 days the ^1H n.m.r. spectrum was identical to that recorded immediately after mixing, corresponding entirely to a mixture of starting materials.

Reaction between cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ and PMe_2Ph.

A $CDCl_3$ solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ was introduced to an n.m.r. tube, and PMe_2Ph (1 mol equiv) was added. The

solution was allowed to stand for 24 h, by which time the -OMe signal previously at δ4.92 had vanished. The solvent was removed and the oily residue was crystallised from CH_2Cl_2/hexane solution by cooling to -78°C, giving white crystals of trans-[PtCl(COEt)-$(PMe_2Ph)_2$], m.pt. 128-129°C (ν(CO) 1635 cm^{-1}). (Found: C 40.53, H 4.79, Cl 6.8% Calculated for $C_{19}H_{26}ClOP_2Pt$: C 40.46, H 4.83, Cl 6.3%)

Reaction of cis-[$PtCl_2${C(OMe)Et}(PMe_2Ph)] with PMe_2Ph in the presence of $AgSO_3CF_3$.

To a solution of cis-[$PtCl_2${C(OMe)Et}(PMe_2Ph)] (49.5mg, 0.104 mmol) in $CHCl_3$ ($2cm^3$) was added $AgSO_3CF_3$ (26.3mg, 0.102 mmol). After stirring for 2 min, PMe_2Ph (14.5μl, 0.102 mmol) was introduced and the solution was filtered after 1 h. The solvent was evaporated from the pale yellow filtrate, and the oily residue was crystallised from CH_2Cl_2/Et_2O by cooling to -78°C to obtain white crystals of trans-[PtCl{C(OMe)Et}$(PMe_2Ph)_2]^+$ $SO_3CF_3^-$, m.pt. 120-122°C. (Found: C 34.79, H 4.18, Cl 4.75% Calculated for $C_{21}H_{30}ClF_3O_4P_2PtS$: C 34.64, H 4.16, Cl 4.87%)

In a similar experiment, cis-[$PtCl_2${C(OEt)Et}(PMe_2Ph)] (28.0mg, 0.057 mmol) and $AgSO_3CF_3$ (14.7mg, 0.057 mmol) were stirred in $CDCl_3$, and PMe_2Ph (8.1μl, 0.057 mmol) was added. After 14 h the phosphine methyl signal was a 1:2:1 triplet. The solution was filtered and the solvent was removed. Crystallisation from CH_2Cl_2/Et_2O gave white crystals of trans-[PtCl{C(OEt)Et}$(PMe_2Ph)_2]^+$ $SO_3CF_3^-$, m. pt. 149-151°C. (Found: C 35.82, H 4.13% Calculated for $C_{22}H_{32}ClF_3O_4P_2PtS$: C 35.60, H 4.35%)

trans-Chloro(methoxyphenylcarbene)bis(triethylphosphine)platinum trifluoromethanesulphonate:

To a solution of trans-[PtCl(COPh)$(PEt_3)_2$] (1.147g, 2.01 mmol) in chloroform ($50cm^3$) was added $MeSO_3CF_3$ ($0.23cm^3$, 2.02 mmol), and

the solution was stirred for 48 h. The solvent was removed to leave an orange-brown oil which solidified on standing. This was dissolved in methanol and, after filtration, the addition of diethyl ether caused precipitation of colourless crystals of trans-$[PtCl\{C(OMe)Ph\}(PEt_3)_2]^+ SO_3CF_3^-$ (0.688g, 47%), m.pt. 126-127°C. (Found: C 34.16, H 5.16, Cl 4.89% Calculated for $C_{21}H_{38}ClF_3O_4P_2PtS$: C 34.26, H 5.21, Cl 4.82%)

Similar reactions were carried out using $MeSO_3F$ or $Me_3O^+ PF_6^-$, instead of $MeSO_3CF_3$, as methylating agent. Related ionic carbene complexes were produced in each case, but the yields were poorer than above.

Treatment of a chloroform solution of trans-$[PtCl(COEt)(PMe_2Ph)_2]$ with $MeSO_3CF_3$ allowed isolation of trans-$[PtCl\{C(OMe)Et\}(PMe_2Ph)_2]^+ SO_3CF_3^-$, which was identified by comparison of its ir. and n.m.r. spectra with those of an authentic sample.

Reaction of cis-$[PtCl_2\{C(OEt)Pr^n\}(PEt_3)]$ with $MeSO_3CF_3$.

Two drops of $MeSO_3CF_3$ were added to a $CDCl_3$ solution of cis-$[PtCl_2\{C(OEt)Pr^n\}(PEt_3)]$ in an n.m.r. tube. After 24 h the presence of MeCl was evident in the ^1H n.m.r. spectrum. After 96 h the volatile fraction was transferred under vacuum to another vessel. The n.m.r. spectrum showed the presence of $EtSO_3CF_3$ (δ4.7 quartet, J 7 Hz; δ1.6 triplet, J 7 Hz), by comparison with an authentic sample.

In a similar experiment cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (18.7mg, 0.039 mmol) was dissolved in $CDCl_3$($0.5cm^3$) and $EtSO_3CF_3$ (5.1μl, 0.040 mmol) was added. After 6 days the ^1H n.m.r. spectrum showed the presence of EtCl, as well as several other peaks in the δ3.0-4.5 region. One of these corresponded to the singlet produced by $MeSO_3CF_3$. The -OMe signal had diminished considerably. The

solution ir. spectrum at this stage showed an intense band at 1654 cm^{-1} due to the formation of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$.

Reaction of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ with $MeSO_3CF_3$, followed by $Et_4N^+ Cl^-$.

To a solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (ca 20mg) in $CDCl_3$ was added $MeSO_3CF_3$ (two drops). The ^1H n.m.r. -OMe signal, originally at δ4.92, was replaced by a new signal at ca δ5.1 (slightly broadened), and a strong singlet at δ3.0, due to MeCl, was observed after 24 h. The solvent was removed and excess $MeSO_3CF_3$ pumped away. The residue was dissolved in fresh $CDCl_3$ and excess $Et_4N^+ Cl^-.H_2O$ was added. The 1:4:1 triplet was then observed at δ4.9, due presumably to regeneration of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$.

Reaction of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ with $AgSO_3CF_3$, followed by PMe_2Ph.

To a $CDCl_3$ solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (17.6mg, 0.037 mmol) was added $AgSO_3CF_3$ (9.5mg, 0.037 mmol), and after 1.5 h the precipitated AgCl was filtered off. The ^1H n.m.r. spectrum exhibited a broadened -OMe signal at δ5.1. Dimethylphenylphosphine (5.3μl, 0.037 mmol) was introduced, and after 21 h the n.m.r. spectrum showed a broadened triplet at δ4.8, and a 1:2:1 triplet in the phosphine methyl region, indicating the formation of trans-$[PtCl\{C(OMe)Et\}(PMe_2Ph)_2]^+ SO_3CF_3^-$ (by comparison with an authentic sample).

Reaction of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ with $Me_3O^+ PF_6^-$.

A $CDCl_3$ solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (39.7mg, 0.083 mmol) was introduced to an n.m.r. tube containing $Me_3O^+ PF_6^-$ (17.0mg, 0.083 mmol), and the tube was sealed. After 3 h MeCl and Me_2O were evident from the ^1H n.m.r. spectrum. After 5 days quantitative reaction had occurred, and the -OMe signal of the

starting complex had been replaced by a broadened signal at δ5.1. The ^{19}F n.m.r. spectrum was recorded after 12 days and showed the presence of PF_6^-, PF_5, POF_3 and SiF_4. Removal of the solvent and crystallisation of the residue from $MeOH/Et_2O$ produced crystals of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, m. pt. 137-138°C (ir. spectrum identical to that of an authentic sample).

Similarly, treatment of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (27.7mg, 0.058 mmol) with $AgSbF_6$ (19.9mg, 0.058 mmol) in $CDCl_3$ solution produced a new signal at δ5.0 in the ^1H n.m.r. spectrum. After filtration and solvent removal, treatment with $MeOH/Et_2O$ gave a pale brown solid, which was identified as $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ by comparison of its ir. spectrum with that of an authentic sample.

Treatment of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ with $AgPF_6$ and $(MeO)_3PO$.

To a $CDCl_3$ solution of cis-$[PtCl_2\{C(OMe)Et\}(PMe_2Ph)]$ (43.4mg, 0.091 mmol) was added $AgPF_6$ (24.9mg, 0.098 mmol). After filtration the ^1H n.m.r. spectrum showed a broadened signal at δ5.1, and $(MeO)_3PO$ (5.0μl, 0.044 mmol) was introduced. After 7 days the n.m.r. spectrum showed that no reaction of $(MeO)_3PO$ had taken place.

Treatment of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ with BCl_3.

Boron trichloride (ca 0.5cm^3) was added to a CH_2Cl_2 solution of cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$ (0.55g, 1.02 mmol) under nitrogen, and the solution was stirred at 0°C for 8 h. The solvent was removed to leave a white, powdery solid. Treatment with CH_2Cl_2/Et_2O resulted in precipitation of a light brown solid (93mg), which was identified from its ir. spectrum as cis-$[PtCl_2\{C(OMe)CH_2Ph\}(PMe_2Ph)]$. After solvent removal the ir. spectrum of the residue showed two bands between 2000 and 2200 cm^{-1}. Several attempts were made to purify this residue, including crystallisations from CH_2Cl_2/Et_2O, $CHCl_3$/hexane, and MeOH/hexane, but no identifiable material could be isolated.

CHAPTER THREE

Reactions of Platinum Carbonyl Complexes

Introduction.

There has been considerable interest in the insertion of carbon monoxide into metal-carbon bonds since the discovery of the first reaction of this type in 1957.[142] Carbonyl insertion reactions have been the subject of a number of reviews in the intervening years,[135-137] much interest being generated in their implication in catalytic processes. These include the hydroformylation of olefins,[19] and the syntheses of acetic acid from methanol[189] and of acrylic acid from acetylene.[190] It should be pointed out that the term "carbonyl insertion" is one in common usage, and is generally used without any attached mechanistic implications.

Carbonyl insertion reactions at platinum.

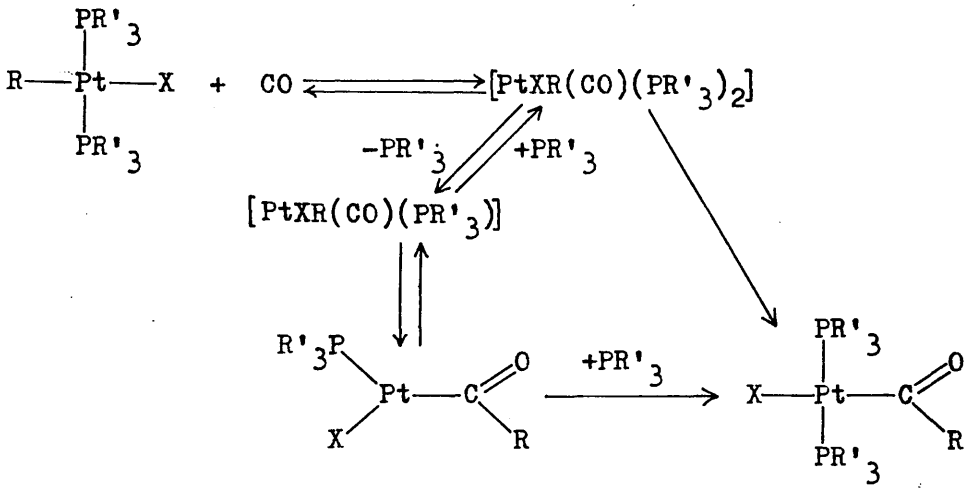
The first examples of such reactions were carried out by Booth and Chatt in 1966, who treated solutions of organoplatinum complexes with high pressures of carbon monoxide:[144]

$$\underline{\text{trans}}\text{-}[PtClMe(PEt_3)_2] + CO \longrightarrow \underline{\text{trans}}\text{-}[PtCl(COMe)(PEt_3)_2]$$

The authors suggested that the production of such acylplatinum complexes might involve five- or six-coordinate intermediates.[144a] This reaction has been the subject of a more recent kinetic investigation, and the implication of five-coordinate species has again been suggested.[191] Kinetic studies by Mawby and coworkers on the conversion of alkyl(carbonyl)platinum species into acylplatinum complexes by nucleophile addition were consistent with a two-step mechanism involving initial carbonyl insertion to yield a three-coordinate intermediate:[192]

$$[PtClEt(CO)(AsPh_3)] \longrightarrow [PtCl(COEt)(AsPh_3)] \xrightarrow{+L} [PtCl(COEt)(AsPh_3)L]$$

Such species were also postulated as intermediates in the carbonylation of trans-$[PtXR(PR'_3)_2]$, and an overall reaction scheme for this process has been proposed (Scheme 2).[191]



Scheme 2

Treatment of cis-$[PtCl_2(CO)(PR_3)]$ complexes with diorganomercurials was found to produce halide-bridged, dimeric acylplatinum complexes:[186]

$$2\text{cis-}[PtCl_2(CO)(PBu_3)] + 2HgPh_2 \xrightarrow{-2PhHgCl} [Pt_2(\mu\text{-}Cl)_2(COPh)_2(PBu_3)_2]$$

Similar complexes have been prepared recently by the action of aryltrimethyltin species on the parent carbonylplatinum compounds.[193]

Acylplatinum complexes tend to undergo decarbonylation when heated for prolonged periods.[144,186] Decarbonylation may also be achieved by creation of a vacant coordination site by halide abstraction:[194]

$$[PtCl(COR)(PPh_3)_2] + AgPF_6 \longrightarrow [PtR(CO)(PPh_3)_2]^+ PF_6^- + AgCl$$

This is essentially the reverse of the reaction of a carbonylplatinum complex with a nucleophile to produce an acylplatinum

compound, and hence may proceed via a three-coordinate intermediate, although a concerted process has also been suggested.[194]

Platinum carbonyl complexes - preparation and bonding.

Most carbonyl complexes of platinum contain the divalent metal, zerovalent metal complexes, though known, being more difficult to handle. Though complexes of the type $[PtCl_2(CO)_2]$ have been prepared,[195] the most commonly encountered species also contain tertiary phosphines or arsines as supporting ligands, as in cis-$[PtCl_2(CO)(PEt_3)]$ and trans-$[PtCl(CO)(AsMe_3)_2]^+ PF_6^-$.

Ionic complexes have been prepared by displacement of halide by carbon monoxide:[196]

$$2[PtCl_2(PEt_3)_2] + 4BF_3 \longrightarrow [Pt_2(\mu\text{-}Cl)_2(PEt_3)_4] (BF_4)_2 + \{BF_2Cl\}$$

$$\xrightarrow{+CO} \text{trans-}[PtCl(CO)(PEt_3)_2]^+ BF_4^-$$

A similar result, under milder conditions, was achieved by treatment of the complex with carbon monoxide in the presence of sodium perchlorate:[197]

$$[PtCl_2(PEt_3)_2] + CO \xrightarrow{NaClO_4} \text{trans-}[PtCl(CO)(PEt_3)_2]^+ ClO_4^-$$

Carbonyl complexes may also be prepared by displacement of an olefin or acetylene by carbon monoxide:[198]

$$K[PtCl_3(C_2H_4)] + CO \longrightarrow K[PtCl_3(CO)] \xrightarrow{PR_3} \text{cis-}[PtCl_2(CO)(PR_3)]$$

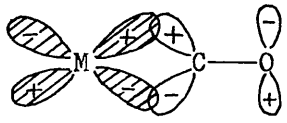
The most widely-used route to neutral carbonyl complexes, however, involves cleavage by carbon monoxide of halide bridges in dimeric platinum complexes, such reactions invariably producing

compounds of cis-configuration as crystalline solids:[55,198]

$$[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2] + 2CO \longrightarrow 2\underline{cis}\text{-}[PtCl_2(CO)(PEt_3)]$$

The bonding in metal carbonyl complexes may conveniently be considered to be of two components; namely, σ-donation from the ligand to the metal and π-backbonding in the reverse direction:

C→M σ-donation



M→C π-backbonding

The existence of this second element accounts for the previously noted shortening of the metal-carbon bond as compared with that in a corresponding alkylmetal complex, and explains the decrease in C-O stretching frequency in metal carbonyl complexes from the value for free carbon monoxide.

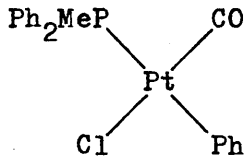
Results and discussion.

Preparation of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$.

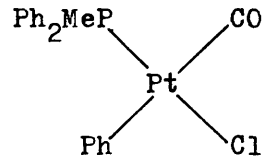
Treatment of a chloroform solution of cis-$[PtCl_2(CO)(PMePh_2)]$ with diphenylmercury at room temperature produced, after removal of phenylmercuric chloride by sublimation, the chloride-bridged, dimeric benzoylplatinum complex, $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, as a colourless, crystalline solid. The infrared spectrum of the solid exhibited a strong band at 1635 cm^{-1}, indicative of an aroylplatinum complex.[144b] When the complex was dissolved in chloroform, however, the solution ir. spectrum showed a band at 2087 cm^{-1} in addition to that at 1635 cm^{-1}. When the solvent was removed only the dimeric aroylplatinum complex was obtained as a solid. The absorption at 2087 cm^{-1} is typical of a terminal carbonyl complex. Thus, in

solution $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ is in equilibrium with one isomer of $[PtClPh(CO)(PMePh_2)]$, although crystallisation of the dimer occurs more readily, presumably due to its lower solubility. ^1H N.m.r. measurements also indicated the presence of more than one species in solution.

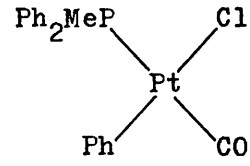
There exist three possible isomers of $[PtClPh(CO)(PMePh_2)]$:



I



II

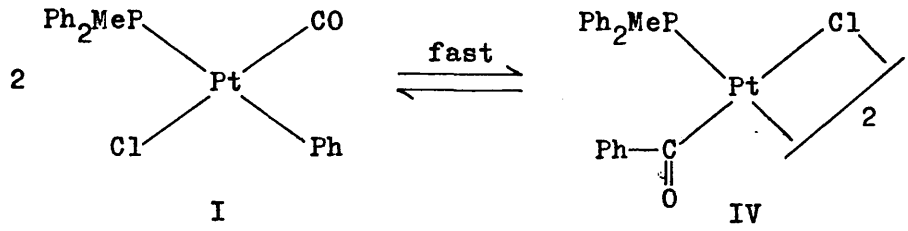


III

Only one isomer was found in solution with the aroyl complex, and its identification was achieved using ^{13}C and ^{31}P n.m.r. spectroscopies. The ^{31}P n.m.r. spectrum showed the presence of a species with a low value of $^1J(Pt\text{-}P)$ (1402 Hz). Such a low value is typical of tertiary phosphine *trans* to a ligand of high *trans*-influence, such as an alkyl or aryl group,[199] and establishes the geometry as that of isomer I. The ^{13}C n.m.r. spectrum of a sample prepared from enriched ^{13}CO was compatible with this assignment, showing parameters typical of CO *trans* to halide and *cis* to tertiary phosphine [200] (δC 162.1 p.p.m., $^1J(Pt\text{-}C)$ 1947 Hz, and $^2J(P\text{-}C)$ 8.2 Hz).

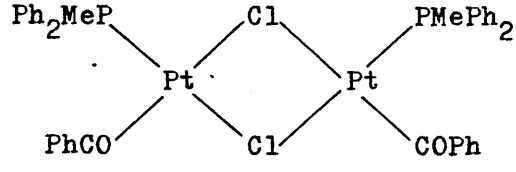
Equilibration of the aroylplatinum dimer with isomer I only is consistent with organic group migration as the mechanism of carbonyl insertion. Such migration would be facilitated for this isomer of $[PtClPh(CO)(PMePh_2)]$, due to the bond-weakening effect of tertiary phosphine in the *trans*-position.

Since rapid solvent removal still produced only the chloride-bridged aroylplatinum dimer, $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, as a solid, it seemed that the two species were in rapid equilibrium:

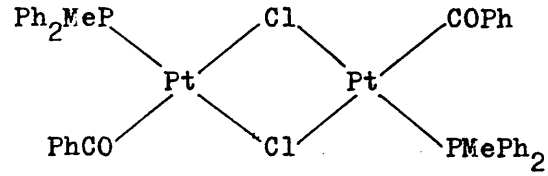


I IV

In fact, cooling the solution to -60°C resulted in the resolving of two signals for IV in the ^{31}P n.m.r. spectrum. These were due to the existence of cis- and trans-isomers:



IV; cis



IV; trans

Isomerisation is sufficiently rapid at room temperature, however, that only one broadened signal is observed. The existence of cis and trans halide-bridged platinum dimers has been recognised in the last few years to be relatively common.[193,201,202]

The equilibrium position between I and IV did not change significantly when chloroform was replaced by benzene or tetrahydrofuran. This is in keeping with the kinetic results of Heck[191] and Mawby[192,203], and suggests that carbonyl insertion and dimerisation are not significantly solvent-assisted, and that solvation of one species is not markedly greater than that of the others.

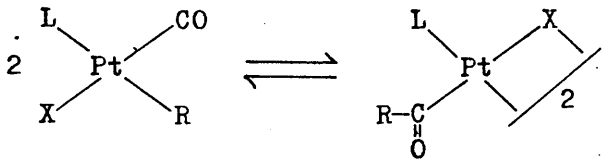
When cis-$[PtCl_2(CO)(PMePh_2)]$ and $HgPh_2$ were mixed in chloroform solution at -60°C no reaction occurred. After warming to -40°C for two hours the ^{31}P n.m.r. spectrum showed the presence of cis-$[PtCl_2(CO)(PMePh_2)]$ and $[PtClPh(CO)(PMePh_2)]$ (I) only. On warming to room

temperature the I/IV equilibrium mixture was obtained. Thus it is apparent that reaction takes place initially to form I which equilibrates in solution to give IV, and not vice-versa.

Complete carbonyl insertion could be achieved by the addition of a nucleophile to solutions containing the I/IV equilibrium mixture. The addition of a stoichiometric amount of $PMePh_2$ to solutions of I and IV allowed almost quantitative recovery of the mononuclear aroylplatinum complex, trans-$[PtCl(COPh)(PMePh_2)_2]$.

Factors affecting the I/IV equilibria.

The general I/IV equilibrium may be written:



It is affected by variations of the ligands R, X and L. Preparation of three series of complexes, by keeping two ligands constant while varying the third, has allowed independent study of the effects of each of these ligands on the equilibrium position.

(i) Variation of the organic group, R.

When cis-$[PtCl_2(CO)(PMePh_2)]$ is treated with HgR_2 (R = Me, Et or CH_2Ph) a reaction analogous to that with diphenylmercury takes place. The position of equilibrium between I and IV, however, varies markedly. For the reaction

$$2[PtClR(CO)(PMePh_2)] \rightleftharpoons [Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$$

the equilibrium constants, K_c, decrease in the order

R = Et (3400) > Ph (160) > Me (8.0) > CH_2Ph (ca 0) ($l\ mol^{-1}$)

^{1}H and ^{31}P n.m.r. and ir. spectroscopic parameters for the complexes $[PtClR(CO)(PMePh_2)]$ (isomer I)

R	δCH_3 (ppm)	$^{2}J(P-H)$ (Hz)	$^{3}J(Pt-H)$ (Hz)	δP (ppm)	$^{1}J(Pt-P)$ (Hz)	$\nu(CO)$ (cm^{-1})
Ph	2.28	9.8	15.2	6.8	1402	2087
Et				12.1	1449	2075
Me	2.21	9.3	15.3	12.1	1449	2079
CH_2Ph	2.18	10.2	15.8	8.4	1414	2077

^{1}H and ^{31}P n.m.r. and ir. spectroscopic parameters for the complexes $[Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$(IV)

R	δCH_3 (ppm)	$^{2}J(P-H)$ (Hz)	$^{3}J(Pt-H)$ (Hz)	δP (ppm)	$^{1}J(Pt-P)$ (Hz)	$\nu(CO)$ (cm^{-1})
Ph	1.84	11.1	63	-3.3	5321	1635
Et	1.99	11.1	63	-1.2	5559	1662
Me	2.00	11.1		-1.2		1660

Table 4

When R = Et or Me, as when R = Ph, the acyl derivatives IV were isolated as crystalline solids from the equilibria. With R = CH_2Ph, however, only I could be detected in solution and $[PtCl(CH_2Ph)(CO)(PMePh_2)]$ was recovered from the solution as a crystalline material. The geometry of each of these mononuclear species (all have R trans to $PMePh_2$) was again established by ^1H and ^{31}P n.m.r. spectroscopy (Table 4).

Infrared intensity measurements were carried out on chloroform solutions of these complexes over the temperature range 0 to 50°C. By calculating equilibrium constants at each temperature for the reaction

$$2[PtClR(CO)(PMePh_2)] \rightleftharpoons [Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$$

and using the relation

$$\Delta G = -RT\ln K_p, \quad \text{where } K_p = \frac{K_c}{RT} = \frac{1}{RT}\,\frac{[\text{dimer}]}{[\text{monomer}]^2}$$

it was possible to construct graphs of ΔG against temperature. Hence ΔH and ΔS were obtained, the values being given in Table 4a.

Enthalpy and entropy values for the reaction

$$2[PtClR(CO)(PMePh_2)] \rightleftharpoons [Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$$

R	ΔH(kJ mol^{-1})	ΔS(J deg^{-1} mol^{-1})
Et	-61.7	-203
Ph	-39.5	-153
Me	-32.0	-155

Table 4a

The large, negative values of ΔS were expected since the reaction involves combination of two species to give one product molecule, that is, an increase in order of the system. The negative ΔH values indicate the favourability of the reaction as written, and their magnitudes obviously reflect the equilibrium positions observed at room temperature. There are little data of this nature in the literature, one example, however, being the decarbonylation of $[PtCl(COR)(PPh_3)_2]$:[204]

$$(Ph_3P)_2ClPt{-}C(=O){-}R\ (cryst.) \longrightarrow (Ph_3P)_2ClPt{-}R\ (cryst.) + CO(g)$$

For R = Ph, a ΔH value of 33.9 ± 1.4 kJ mol^{-1} was found for this process.[204] It was not possible, however, to obtain ΔH for the decarbonylation step itself and, in this work, the ΔH values (Table 4a) refer to a combination of the carbonyl insertion and dimerisation steps.

Addition of tertiary phosphine to I/IV equilibria produced the corresponding acylbis(tertiary phosphine)platinum complexes. For R = Me or Et, the formation of the complexes trans-$[PtCl(COR)(PMePh_2)_2]$ was observed by ^{13}C n.m.r. spectroscopy. Slow addition of $PMePh_2$ to a benzene solution of $[PtCl(CH_2Ph)(CO)(PMePh_2)]$ similarly allowed isolation of trans-$[PtCl(COCH_2Ph)(PMePh_2)_2]$, but rapid addition caused CO loss, the ir. spectrum of the resulting solid showing almost total absence of absorptions in the 2100 and 1600 cm^{-1} regions. The fact that acylplatinum products are obtained with R = CH_2Ph, despite the detection of I only in solution initially, suggests that a I/IV equilibrium does exist and IV is readily attacked by $PMePh_2$ to produce trans-$[PtCl(COCH_2Ph)(PMePh_2)_2]$. (This attack could be on the three-coordinate intermediate, $[PtCl(COCH_2Ph)(PMePh_2)]$, which, though not detected, is presumably part of the overall equilibrium sequence.) When IV is in low

concentration compared to the tertiary phosphine, that is, on rapid addition of $PMePh_2$, a slower nucleophilic attack on I successfully competes and leads to CO elimination. Similar effects of the rate of tertiary phosphine addition have been reported by Mawby[205] and Wright,[206] who also noted that trialkylphosphines tended to favour CO elimination over insertion, whereas triarylphosphines favoured insertion. Since trialkylphosphines are generally more nucleophilic than arylphosphines, these observations are compatible with the above interpretation.

The extent of insertion, which decreases in the order Et > Ph > Me > CH_2Ph, remains unexplained at present, although several similar series have emerged from kinetic studies of insertion and decarbonylation reactions at other metals.[136,137]

Preliminary studies of the extent of insertion with substituted aryl groups have given the following order:[207]

$$\underline{p}\text{-}MeOC_6H_4 > \underline{p}\text{-}MeC_6H_4 > \underline{m}\text{-}MeC_6H_4,\ C_6H_5 > \underline{p}\text{-}ClC_6H_4 > \underline{o}\text{-}MeC_6H_4$$

This clearly reflects, at least for the para-substituted aryls, a decrease in electron-donating ability. A similar series was obtained with para-substituted benzyl groups from a kinetic study of the decarbonylation of $[IrCl_2(PPh_3)_2(COCH_2Ar)]$ in benzene solution.[208]

(ii) Variation of the halide, X.

When an acetone solution of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ was treated with a large excess of lithium bromide, lithium iodide or sodium benzylthiolate complete metathetical replacement of chloride resulted. Separation of the platinum species by chloroform/water extraction, followed by crystallisation from a chloroform/diethyl ether mixture, allowed isolation of the bromide- and iodide-bridged aroylplatinum complexes, but the thio-bridged compound resisted

^{31}P n.m.r. and ir. spectroscopic parameters for the complexes $[PtXPh(CO)(PMePh_2)]$ (I)

X	δP/ppm	$^1J(Pt-P)$/Hz	$\nu(CO)/cm^{-1}$
Cl	6.8	1402	2087
Br	2.9	1436	2085
I			2085

^{31}P n.m.r. and ir. spectroscopic parameters for the complexes $[Pt_2(\mu\text{-}X)_2(COPh)_2(PMePh_2)_2]$ (IV)

X	δP/ppm	$^1J(Pt-P)$/Hz	$\nu(CO)/cm^{-1}$
Cl	-3.3	5321	1635
Br	-3.0	5280	1633
	-3.5	5397	
I	-4.4	5016	1630
	-5.1	ca 5100	
SCH_2Ph	-3.8	4048	

all ^{31}P n.m.r. spectra were recorded at 25°C

Table 5

such attempts to purify it.

Solution infrared spectra of the bromide and iodide complexes in chloroform showed absorptions due to both aroyl and terminal carbonyl groups, the latter being very weak for the iodide case, while by ^{31}P n.m.r. spectroscopy only the dimeric aroylplatinum complexes could be observed for X = I or SCH_2Ph. With X = Br, a relatively weak signal due to I ($^{1}J(Pt-P)$ 1436 Hz) was also present.

The ^{31}P n.m.r. spectra of the bromide and iodide complexes, recorded at room temperature, each showed two signals for the halide-bridged aroylplatinum dimers due to the existence of cis- and trans-isomers. The sharp signals obtained suggest that cis-trans isomerisation is slow, relative to the n.m.r. timescale, at this temperature. The thio-bridged complex showed considerably broadened signals, but the existence of two distinct signals was not established. The ^{31}P n.m.r. and ir. data are given in Table 5.

The extent of insertion is dependent on the halide or pseudo-halide involved, and decreases in the following order:

$$SCH_2Ph \text{ (ca 100\%)} > I \text{ (98\%)} > Br \text{ (90\%)} > Cl \text{ (60\%)}$$

This reflects the strength of the platinum-halide bridge.[45,54] Thus, if the overall equilibrium is the result of carbonyl insertion and dimerisation steps, it seems likely that the effect of a change of halide is centred on the dimerisation step. The groups which form the strongest bridges, that is, iodide and benzylthiolate, thus increase the extent of insertion.

(iii) Variation of the neutral ligand, L.

The complexes cis-$[PtCl_2(CO)L]$ (L = PEt_3, PMe_2Ph, PPh_3, $AsMePh_2$ or $AsPh_3$) were prepared by passing carbon monoxide through benzene solutions of the chloride-bridged dimers, $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$. For

L = PCy_3 or P(o-tolyl)$_3$ the chloride-bridged dimers are unknown, so this method of preparation was not available. The complexes cis-$[PtCl_2(CO)L]$ (L = PCy_3 or P(o-tolyl)$_3$) were prepared, therefore, by introducing the tertiary phosphine to chloroform solutions of $[PtCl_2(norbornadiene)]$, which had previously been saturated with carbon monoxide, and maintaining a stream of the gas through the system during the course of the reaction.

Reaction of cis-$[PtCl_2(CO)L]$ (L = PEt_3, PMe_2Ph or PPh_3) with $HgPh_2$ in chloroform solution resembled closely that for cis-$[PtCl_2(CO)(PMePh_2)]$. In each case, the isolated product was the chloride-bridged benzoylplatinum complexes, $[Pt_2(\mu\text{-}Cl)_2(COPh)_2L_2]$. In chloroform solution these complexes were found to be in equilibrium with the corresponding complex, [PtClPh(CO)L]. The low $^1J(Pt\text{-}P)$ values obtained from their ^{31}P n.m.r. spectra indicated that isomer I was involved in every case. When L = PCy_3 the reaction with $HgPh_2$ proceeded analogously, with both I and IV being observed in solution. Crystallisation of the product resulted in a mixture of I and IV, and the chloride-bridged benzoylplatinum complex could not be obtained alone.

A similar reaction takes place between cis-$[PtCl_2(CO)L]$ (L = P(o-tolyl)$_3$, $AsMePh_2$ or $AsPh_3$) and $HgPh_2$. In these cases, however, only [PtClPh(CO)L] could be observed in solution, ir. and n.m.r. spectral examinations failing to detect any chloride-bridged dimer. The low value of $^1J(Pt\text{-}P)$ for [PtClPh(CO){P(o-tolyl)$_3$}] (1366 Hz) again proves its geometry to be that of isomer I. The values of $\nu(CO)$, and ^{13}C n.m.r. data for ^{13}CO-containing samples, for the arsine complexes are typical of complexes with this geometry. The tri-o-tolylphosphine complex, [PtClPh(CO){P(o-tolyl)$_3$}], was isolated as a crystalline solid, but the analogous arsine derivatives tended to decompose on attempted purification. In these cases, slow

^{31}P n.m.r. and ir. spectroscopic parameters for the complexes [PtClPh(CO)L] (I)

L	δP/ppm	^{1}J(Pt-P)	ν(CO)/cm^{-1}	comments
PEt_3	18.9	1407	2077	
PMe_2Ph	-5.3	1381	2083	
$PMePh_2$	6.8	1402	2087	
PPh_3	18.9	1426	2087	
PCy_3	31.0	1437	2072	
$P(o\text{-tolyl})_3$	17.9	1366	2083	
$AsMePh_2$			2084	δC 161.5 ppm, ^{1}J(Pt-C) 1945 Hz
$AsPh_3$			2085	δC 161.6 ppm, ^{1}J(Pt-C) 1943 Hz

^{31}P n.m.r. and ir. spectroscopic parameters for the complexes $[Pt_2(\mu\text{-}Cl)_2(COPh)_2L_2]$ (IV)

L	δP/ppm	^{1}J(Pt-P)/Hz	ν(CO)/cm^{-1}
PEt_3	10.7	5041	1628
PMe_2Ph	-15.0	5180	1631
$PMePh_2$	-3.3	5321	1635
PPh_3	11.0	5495	1639
PCy_3	22.4	5055	1627

Table 6

addition of one molar equivalent of the tertiary arsine produced the benzoylbis(tertiary arsine)platinum complexes, trans-[PtCl-(COPh)L_2] (L = $AsMePh_2$ or $AsPh_3$), which were isolated as crystalline materials. Infrared and n.m.r. data for the complexes I and IV are given in Table 6.

Treatment of the complexes [PtClPh(CO)L] (L = $AsMePh_2$ or $AsPh_3$) with the corresponding tertiary arsine, like the addition of $PMePh_2$ to [PtCl(CH_2Ph)(CO)($PMePh_2$)], are reactions analogous to the nucleophile-assisted insertion reactions studied by Mawby.[192,203,205] The insertion reaction proceeds, therefore, even when the equilibrium position is such that only I can be detected in solution. Addition of P(o-tolyl)$_3$ to a solution of [PtClPh(CO){P(o-tolyl)$_3$}], or of PCy_3 to the corresponding I/IV equilibrium mixture, however, failed to promote insertion, and the solutions remained unchanged at room temperature. This was surprising since the platinum complexes were of the correct geometry for insertion, and the tricyclohexylphosphine complex exists in solution in equilibrium with a detectable amount of the chloride-bridged aroylplatinum dimer. Presumably the excessive steric demand of these tertiary phosphines must prevent attack of another such group at platinum, either on I (which would lead to CO loss), IV or the three-coordinate intermediate.

The extent of insertion, as evidenced by the relative amounts of I and IV observed in solution by ir. and ^{31}P n.m.r. spectroscopies at ambient temperature, is dependent on the nature of L and decreases in the following order:

PEt_3 > PMe_2Ph > $PMePh_2$ > PPh_3 > PCy_3 > P(o-tolyl)$_3$, $AsMePh_2$, $AsPh_3$
(82%) (76%) (60%) (37%) (17%) (0%)

Explanation of this order is not straightforward, and both steric

and electronic factors must be considered. The effective sizes of the ligands can be estimated from the cone angles subtended at the metal atoms, and an extensive series of phosphorus ligand cone angles has been compiled by Tolman,[209] mainly from model measurements. Although it has been shown that this angle is dependent on the system involved,[210] it is apparent that PCy_3 and P(o-tolyl)$_3$ are particularly bulky, and will favour the less sterically crowded side of an equilibrium. These ligands favour I, rather than IV, presumably because CO in the cis-position in I is less sterically demanding than is COPh in IV.

Steric factors alone cannot account for the remainder of the sequence, however, and the overall correlation between equilibrium position and cone angle[209] is poor. The tertiary arsines, which are likely to have small cone angles due to their longer Pt-L bonds, are obviously in an anomalous position. The bond-weakening trans-influence of L would be expected to be important in promoting migration of the phenyl group in the trans-position, since aryl migration is the likely mechanism for the "carbonyl insertion" reaction.[142]

Tolman's "electronic parameter", which provides some measure of the electron-donating ability of the tertiary phosphine,[211] gives a reasonable fit with the observed equilibrium positions for PEt_3, PMe_2Ph, $PMePh_2$ and PPh_3 (though not, of course, for PCy_3 or P(o-tolyl)$_3$), but these parameters refer to tetrahedral $Ni(CO)_3L$ molecules.[211] Spectroscopic[212] and kinetic[213] data on tertiary phosphine and arsine complexes suggest that a trans-influence series would follow the observed pattern of equilibrium positions for the less bulky ligands, but data for the complete series have not been published. In an attempt to compile such a series, ν(Pt-Cl) values were accurately measured for the complexes cis-$[PtCl_2L_2]$ (Table 7).

Infrared spectra for the complexes *cis*-$[PtCl_2L_2]$ and *cis*-$[PtCl_2(CO)L]$, recorded as CsI discs

L	*cis*-$[PtCl_2L_2]$ ν(Pt-Cl)/cm^{-1}	*cis*-$[PtCl_2(CO)L]$ ν(Pt-Cl)/cm^{-1}
PEt_3	303, 280	353, 304
PMe_2Ph	308, 286	349, 301
$PMePh_2$	316, 292	348, 304
PPh_3	318, 293	353, 312
PCy_3		345, 303
$P(o\text{-tolyl})_3$		349, 312 (KBr disc)
$AsMePh_2$	320, 299	350, 308
$AsPh_3$	338, 325 sh	341, 315

Table 7

The values fit the trans-influence order

$$PEt_3 > PMe_2Ph > PMePh_2 > PPh_3 > AsMePh_2 > AsPh_3,$$

which matches the equilibrium position sequence for these ligands. Analogous complexes for L = PCy_3 or P(o-tolyl)$_3$ are not available, trans-$[PtCl_2L_2]$ complexes being preferred for such bulky ligands, but ν(Pt-Cl) values for cis-$[PtCl_2(CO)L]$ complexes, as well as Tolman's values,[211] suggest that these two ligands occupy exceptional positions in the equilibrium series, with PCy_3 electronically resembling PEt_3, and P(o-tolyl)$_3$ being similar in this respect to PPh_3.

It thus appears that the trans-influence alone of the neutral ligand, L, significantly affects the equilibrium position up to some critical ligand size (this size corresponding to a cone angle greater than 145° - the value calculated for PPh_3 - but less than 170° - for PCy_3),[209] whereupon steric effects become important.

Preparation and reactions of isomers II and III.

Addition of two molar equivalents of $HgPh_2$ to benzene solutions of $[Pt_2(\mu\text{-}X)_2X_2L_2]$ (X = Cl, L = PEt_3, PMe_2Ph, $PMePh_2$ or PPh_3; X = Br, L = PMe_2Ph; X = I, L = $PMePh_2$) produced the halide-bridged, dimeric arylplatinum complexes, $[Pt_2(\mu\text{-}X)_2Ph_2L_2]$. The ^{31}P n.m.r. spectra of of these compounds showed them to exist as cis- and trans-isomers. Cleavage of these halide-bridged phenylplatinum complexes by carbon monoxide, in chloroform solution, gave rise to a mixture of two species, each of which gave rise to an absorption in the 2000-2200 cm^{-1} region of the ir. spectrum. (For the dimeric complex with X = I and L = $PMePh_2$, only one species was observed in solution after treatment with carbon monoxide.) The identities of the two complexes, as isomers II and III, were revealed by their ^{13}C and ^{31}P n.m.r.

^{31}P and ^{13}C n.m.r. spectroscopic parameters

for the complexes [PtXPh(CO)L] (isomer II)

L	X	δP/ppm	^{1}J(Pt-P)/Hz	δC/ppm	^{1}J(Pt-C)/Hz	^{2}J(P-C)/Hz
PEt_3	Cl	12.5	3700	178.1	909	6.1
PMe_2Ph	Cl			177.6	906	5.9
PMe_2Ph	Br	-14.4	3770			
$PMePh_2$	Cl	-1.7	3920	177.4	906	6.1
$PMePh_2$	I	-1.6	3699			
PPh_3	Cl	10.2	4071	177.7	895±5	6.3

^{31}P and ^{13}C n.m.r. spectroscopic parameters

for the complexes [PtXPh(CO)L] (isomer III)

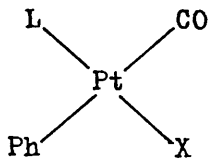
L	X	δP/ppm	^{1}J(Pt-P)/Hz	δC/ppm	^{1}J(Pt-C)/Hz	^{2}J(P-C)/Hz
PEt_3	Cl	12.1	3337	174.4	1352	148.4
PMe_2Ph	Cl			173.8	1390	157.5
PMe_2Ph	Br	-10.1	3359			
$PMePh_2$	Cl	5.7	3481	173.3	1427	157.8
$PMePh_2$	I	a				
PPh_3	Cl	20.1	3561	172.4[b]	1461[b]	155.6[b]

(a) not observed

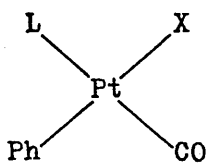
(b) at -60°C

Table 8

spectra (Table 8).



II



III

The relatively high $^{1}J(Pt-P)$ values, compared with those for isomer I, are indicative of tertiary phosphine trans to ligands of low trans-influence. For samples prepared from enriched ^{13}CO the ^{13}C n.m.r. spectra were very informative. The low $^{1}J(Pt-C)$ values for II are consistent with CO being trans to the organic group, and cis to tertiary phosphine.[200] The very large values of $^{2}J(P-C)$ for III were expected for CO trans to tertiary phosphine, since large ^{2}J values are well-known for hydride[214] or tertiary phosphine[95] trans to tertiary phosphine. Such species with CO trans to tertiary phosphine, however, had not previously been studied.

When carbon monoxide was passed through a chloroform solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ at -60°C the ^{31}P n.m.r. spectrum, recorded at that temperature, showed almost quantitative reaction to give III, with only a very weak signal due to isomer II being detected. On warming, however, the two isomers equilibrated and, after standing at room temperature for 24 hours, the final equilibrium mixture was reached when II and III were present in the ratio 5.5:1. This effect could also be observed for the same complexes by solution ir. spectroscopy, the absorption at 2116 cm^{-1}, due to III, gradually being replaced by another at 2106 cm^{-1} until the former was only present as a shoulder on the 2106 cm^{-1} peak.

A crystalline solid was isolated from a benzene solution of $[PtClPh(CO)(PMePh_2)]$ (II and III). This had a strong $\nu(CO)$ at 2095 cm^{-1}, and a platinum-chlorine stretching frequency of 308 cm^{-1}.

This is indicative of chloride trans to tertiary phosphine,[215] suggesting that the crystalline material was isomer II. If the composition of the solid reflected the equilibrium observed in solution, however, it is doubtful whether the smaller amount of III would be easily detected. When this solid was re-dissolved in chloroform, the ^{31}P n.m.r. spectrum after one hour showed the ratio of II:III to be 6.6:1. While II and III isomerise on standing, after 21 hours neither isomer I nor the associated chloride-bridged aroyl-platinum complex, IV, was observed. It is thus apparent that isomers II and III of $[PtClPh(CO)(PMePh_2)]$ do not undergo rapid CO insertion analogous to isomer I, and that the isomerisation process linking II and III does not convert them to I.

When phenyl-lithium was slowly added to a benzene solution of cis-$[PtCl_2(CO)(PMePh_2)]$ under an atmosphere of carbon monoxide, a complex mixture of products resulted. The solution ir. spectrum exhibited several bands in the 2000-2200 cm^{-1} region, and the ^{31}P n.m.r. spectrum of a similar reaction mixture in $CDCl_3$ solution showed the presence of isomer II (δP -1.7 p.p.m., $^1J(Pt-P)$ 3919 Hz), as well as trans-$[PtClPh(PMePh_2)_2]$ (δP 8.7 p.p.m., $^1J(Pt-P)$ 3010 Hz) and trans-$[PtCl(COPh)(PMePh_2)_2]$ (δP 5.1 p.p.m., $^1J(Pt-P)$ 3213 Hz). Detection of III was not possible due to overlap of another, unidentified signal, but the spectrum showed no trace of isomer I or the benzoylplatinum dimer, IV. Previous reactions of cis-$[PtCl_2(CO)(PPh_3)]$ with methyl-lithium,[186] and cis-$[PtCl_2(CO)(PEt_3)]$ with phenyl-lithium,[216] were also complicated, with no isolable products. In the latter case, considerable benzophenone was produced, perhaps indicative of attack of a second phenyl-lithium molecule, but no benzoylplatinum species were detected. The production of bis(diphenyl-methylphosphine)platinum species, along with the dark colour of the solutions, suggests that considerable decomposition may have taken

place, but it is not clear whether trans-[PtCl(COPh)($PMePh_2$)$_2$] was produced by attack of free tertiary phosphine on I or IV which may have been transiently present, or by some other route.

Garrou and Heck reported the isolation of two isomers of [PtClPh(CO)(PCy_3)] from the reaction of trans-[PtClPh(PCy_3)$_2$] with carbon monoxide in sym-tetrachloroethane at 70°C over four days.[191] These isomers resisted CO insertion, and their isolation was instrumental in establishing the intermediacy of [PtXR(CO)(PR'_3)] species in a general scheme for the reaction of trans-[PtXR(PR'_3)$_2$] complexes with carbon monoxide. Repetition of the above reaction using labelled ^{13}CO suggested, from periodic ^{13}C and ^{31}P n.m.r. examination, that the reaction was slower and more complicated than had been reported. Some trans-[PtClPh(PCy_3)$_2$] remained after seven days at 70°C and, amongst the many products, considerable amounts of cis-[$PtCl_2$(CO)(PCy_3)] (δP 37.1 p.p.m., ^1J(Pt-P) 2844 Hz) were observed. No trace of isomer I, or the chloride-bridged dimer IV, was detected, but spectroscopic characteristics clearly typical of isomers II and III were found (II: δP 27.8 p.p.m., ^1J(Pt-P) 3725 Hz, ^2J(P-C) 6.8 Hz, δC 178.3 p.p.m., ^1J(Pt-C) 900 Hz; III: δP 15.8 p.p.m., ^2J(P-C) 141.1 Hz, δC 173.0 p.p.m.).

When solutions of [PtClPh(CO)($PMePh_2$)] (II and III) were heated to 50°C for two hours, small amounts (ca 5%) of isomer I and the chloride-bridged benzoylplatinum complex, IV, were detected in the solution ir. spectrum, which also indicated that considerable loss of carbon monoxide had also occurred. A weak aroylplatinum peak at about 1630 cm^{-1} was observed in the ir. spectrum of the solid residue. This spectrum, however, closely resembled that of [$Pt_2(\mu$-Cl)$_2Ph_2$-($PMePh_2$)$_2$], indicating that such treatment predominantly caused loss of carbon monoxide. Allowing chloroform solutions of isomers II and III to stand at ambient temperature for seven days produced some

I and IV, but the main components of the mixture were still isomers II and III of $[PtClPh(CO)(PMePh_2)]$.

In contrast to the above, when a solution of $[PtClPh(CO)(PPh_3)]$ (isomers II and III) was allowed to stand for 24 hours at ambient temperature considerable amounts of I and IV were observed. In fact, this isomerisation occurred sufficiently rapidly to prevent isolation of isomer II (and III) as a crystalline material, uncontaminated by I and IV. Passing carbon monoxide through a chloroform solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PEt_3)_2]$ or $[Pt_2(\mu\text{-}Br)_2Ph_2(PMe_2Ph)_2]$ resulted in a mixture of the corresponding isomers II and III. In each case the solution was unchanged after standing for several days, but total CO loss occurred on evaporation of the solvent or attempted crystallisation. When a solution of $[Pt_2(\mu\text{-}I)_2Ph_2(PMePh_2)_2]$ was treated with carbon monoxide only isomer II of $[PtIPh(CO)(PMePh_2)]$ was observed in solution by ^{31}P n.m.r. spectroscopy. On standing for 44 hours, total loss of carbon monoxide took place to regenerate the starting complex.

Attempts to promote carbonyl insertion at $[PtClPh(CO)(PMePh_2)]$ (II and III) were unsuccessful. Slow addition of one molar equivalent of $PMePh_2$ caused elimination of carbon monoxide, the main product being identified as <u>trans</u>-$[PtClPh(PMePh_2)_2]$.

Whilst the small amounts of $[PtClPh(CO)(PMePh_2)]$ (isomer I) and $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ (IV) produced from solutions of II and III by heating or on standing at room temperature could have been formed by a slow carbonyl insertion reaction of II and/or III, the failure to promote such a reaction by addition of tertiary phosphine makes this seem unlikely. Instead, a slow isomerisation to isomer I is a more probable explanation. Cleavage of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ by CO produces only isomers II and III, so reversible loss of CO from II and/or III can provide an isomerisation route between these

two species. That this does occur was shown by passing a stream of nitrogen gas through a sym-tetrachloroethane solution of [PtClPh-(CO)($PMePh_2$)] (II and III) to sweep out free carbon monoxide. Comparison of the solution ir. spectra with those of an identical standard solution after 7 and 21 hours indicated considerable removal of CO in the former case. Similarly then, reversible loss of tertiary phosphine would provide an isomerisation route between isomers I and III. Such a process would be expected to be slower than isomerisation of II and III, since tertiary phosphines are generally more nucleophilic and more strongly bound to the metal than carbon monoxide. Conversion of isomer I to either II or III has not been detected, however, so it is probable that I is the thermodynamically most stable isomer.

The faster production of isomer I from solutions of [PtClPh-(CO)(PPh_3)] (II and III) is consistent with this isomerisation mechanism. Triphenylphosphine is less nucleophilic than $PMePh_2$, and hence may be more readily liberated. Triethyl- and dimethylphenyl-phosphine are stronger nucleophiles than $PMePh_2$, and hence less prone to elimination, so the complexes [PtClPh(CO)(PEt_3)] (II and III) and [PtBrPh(CO)(PMe_2Ph)] (II and III) show no sign at all of isomerisation to the corresponding isomers I on standing. The loss of CO from [PtIPh(CO)($PMePh_2$)] mentioned above is probably simply due to the nucleophilicity of coordinated iodide and its ability to form strong bridges in the complex $[Pt_2(\mu\text{-}I)_2Ph_2(PMePh_2)_2]$.

It has been shown that the addition of tertiary phosphine to solutions of $[Pt_2(\mu\text{-}Cl)_2(n\text{-}C_8H_{17})_2(CO)_2]$ may cause insertion or elimination of carbon monoxide.[206] Slow addition or the use of less nucleophilic phosphines, such as PPh_3, were found to favour the insertion reaction.[206] These observations are of interest in the context of the foregoing interpretation, since tertiary phosphine

addition would result in the formation of $[PtCl(n\text{-}C_8H_{17})(CO)L]$ (isomers I and III). The action of a further one molar equivalent of tertiary phosphine would be to cause CO insertion at I and elimination at III. The use of PPh_3, or the slow addition of tertiary phosphine, however, would permit a greater degree of isomerisation of III (and/or II, since II and III are likely to exist in dynamic equilibrium) into geometry I, and hence the acylplatinum product:

$$[Pt_2(\mu\text{-}Cl)_2(n\text{-}C_8H_{17})_2(CO)_2] \xrightarrow{2L} \underset{\text{I and III}}{2[PtCl(n\text{-}C_8H_{17})(CO)L]}$$

$$\xrightarrow[\text{slow}]{2L} 2[PtCl(COC_8H_{17})L_2]$$

When chlorine gas was passed through a chloroform solution of $[PtClPh(CO)(PMePh_2)]$ (II and III) for ten minutes, total loss of carbon monoxide was observed from the solution ir. spectrum, and a chloride-bridged, dimeric phenylplatinum(IV) species, $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$, was isolated. This compound was also prepared by addition of chlorine to a solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ in methylene chloride. The ^{31}P n.m.r. spectrum indicated that the material existed in a considerable number of isomeric forms. When carbon monoxide was passed through a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$, the solution ir. spectrum showed a strong absorption at 2115 cm^{-1}, and <u>cis</u>-$[PtCl_2(CO)(PMePh_2)]$ was isolated in fairly high yield, the by-product being, presumably, chlorobenzene:

$$[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2] \xrightarrow{CO} 2\underline{cis}\text{-}[PtCl_2(CO)(PMePh_2)] + 2PhCl$$

It was not ascertained, however, whether during the preparation of $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$, or its subsequent reaction with carbon

monoxide, a carbonylplatinum(IV) complex was formed. As the chloride-bridged platinum(IV) dimer itself did not tend to eliminate chlorobenzene in solution, it seems likely that PhCl loss was induced by nucleophilic attack of carbon monoxide, and that a transient species $[PtCl_3Ph(CO)(PMePh_2)]$ was involved.

Conclusions.

The reaction of diphenylmercury with cis-$[PtCl_2(CO)(PMePh_2)]$ has been proposed to occur via an electrophilic attack on Hg-C (S_E2) or by an oxidative addition/reductive elimination sequence.[117,186] The high trans-influence of tertiary phosphine[89,92] would weaken the platinum-chlorine bond trans to it, favouring its elimination.

The reaction of phenyl-lithium with cis-$[PtCl_2(CO)(PMePh_2)]$ is more likely to proceed via a carbanion attack at platinum to produce a five-coordinate intermediate.[217] It might be expected that the high kinetic trans-effect of carbon monoxide[89,92] would stabilise the trigonal bipyramidal intermediate with the entering and leaving groups in the same trigonal plane as itself. This would result in the formation of isomer II of $[PtClPh(CO)(PMePh_2)]$, and indeed this isomer was detected in the reaction mixtures. The complexity of the spectra produced, however, suggests that two consecutive carbanion attacks on the platinum centre may have occurred in some cases, and the production of bis(tertiary phosphine)platinum complexes is likely to have involved elimination of tertiary phosphine from other molecules. Thus it is not clear if initial LiPh attack on cis-$[PtCl_2(CO)(PMePh_2)]$ always produced isomer II, which may partially have undergone further reaction, or if the results of the carbanion attack were more random.

The detailed mechanism of carbonyl insertion has been elucidated in only a few cases, and has been found to involve migration of the organic group to a neighbouring CO ligand already present in the

Equilibrium constants for the reaction

$2[PtXR(CO)L] \rightleftharpoons [Pt_2(\mu\text{-}X)_2(COR)_2L_2]$

and the relative amounts of I and IV

expressed as percentage composition

for 0.02 M solutions at 25°C

L	X	R	K_c/1 mol^{-1}	I/%	IV/%
$PMePh_2$	Cl	Ph	160	40	60
$PMePh_2$	Cl	Et	3400	10	90
$PMePh_2$	Cl	Me	8.0	83	17
$PMePh_2$	Cl	CH_2Ph	0	100	0
$PMePh_2$	Br	Ph	3600	10	90
$PMePh_2$	I	Ph	9.6×10^4	2	98
$PMePh_2$	SCH_2Ph	Ph		ca 0	ca 100
PEt_3	Cl	Ph	690	18	82
PMe_2Ph	Cl	Ph	650	24	76
PPh_3	Cl	Ph	31	63	37
PCy_3	Cl	Ph	8.1	83	17
$P(o\text{-tolyl})_3$	Cl	Ph	0	100	0
$AsMePh_2$	Cl	Ph	0	100	0
$AsPh_3$	Cl	Ph	0	100	0

Table 9

coordination sphere of the metal.[136,137] This mechanism has not been proved to operate for carbonyl insertion reactions at platinum, but it is fully consistent with the observations for the complexes described here. In isomer I the organic group lies trans to tertiary phosphine or arsine. The high trans-influence of tertiary phosphine[89,92] would labilise the platinum-carbon bond, and hence promote migration of the organic group. In isomer III the organic group lies trans to halide and the platinum-carbon bond would not be labilised, while isomer II does not have the cis-arrangement of R and CO necessary for insertion. Thus it is found that only in isomer I does organic group migration take place, the extent of insertion being dependent to a considerable extent on the trans-influence of the neutral trans-ligand. Equilibrium constants and percentage compositions at equilibrium of all the I/IV systems described, obtained from solution infrared spectral measurements, are given in Table 9.

Finally, it may be noted that preliminary kinetic investigations have produced equilibrium constants close to those obtained from infrared spectral data for a number of the I/IV equilibria,[218] and have suggested that calculation of separate rate constants for the carbonyl insertion and dimerisation steps may be possible.

Experimental.

Infrared spectra of solid samples as KBr discs were recorded on Perkin Elmer 225 and 580 spectrophotometers. Infrared spectra of solutions were recorded on a Perkin Elmer 577 instrument, using 0.5mm NaCl solution cells. Standard calibration graphs were constructed over the 0.005 to 0.100M concentration range for the complexes cis-$[PtCl_2(CO)(PMePh_2)]$ and trans-$[PtCl(COPh)(PMePh_2)_2]$. Intensity measurements for I/IV equilibria were related to these curves and equilibrium constants were calculated. Variable temperature spectra

were obtained using 0.5mm NaCl cells mounted in Beckman VLT-2 cell holders, the temperature being maintained by means of a water jacket.

^{1}H N.m.r. spectra were recorded in $CDCl_3$ solution using a Perkin Elmer R32 spectrometer (90 MHz), and ^{13}C and ^{31}P n.m.r. spectra were obtained from a Varian XL-100 instrument operating in the Fourier Transform mode. Microanalyses were performed by Alfred Bernhardt, West Germany.

The complexes cis-$[PtCl_2(CO)L]$ (L = PEt_3, PMe_2Ph, $PMePh_2$ or PPh_3) were prepared by passing carbon monoxide through suspensions of $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$ in benzene, the complexes being obtained as colourless crystals.

Di-μ-chlorodibenzoylbis(diphenylmethylphosphine)diplatinum: cis-$[PtCl_2(CO)(PMePh_2)]$ (1.965g, 3.98 mmol) was dissolved in chloroform (100cm^3) under nitrogen, and diphenylmercury (1.413g, 3.98 mmol) was added. The solution became yellow and a fine, colourless solid precipitated. The solution was stirred for 4 h and the precipitate of phenylmercuric chloride (0.959g) was filtered off. After the solvent had been evaporated, the remaining PhHgCl was removed by sublimation at 80°C/0.001 torr for 7 h. The residue was crystallised from benzene/pet. ether (40-60°) to yield colourless crystals of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, m.pt. 232-235°C (decomp.). (Found: C 44.66, H 3.33% Calculated for $C_{40}H_{36}Cl_2O_2P_2Pt_2$: C 44.82, H 3.39%)

The following were prepared similarly, except that the reactions involving diethyl-and dimethylmercury were carried out in benzene under a CO atmosphere, with heating to 50°C for 1 h in the latter case.

Di-μ-chlorodipropionylbis(diphenylmethylphosphine)diplatinum: m.pt. 153-157°C. (Found: C 39.31, H 3.50% Calculated for $C_{32}H_{36}Cl_2O_2P_2Pt_2$: C 39.38, H 3.41%)

Di-μ-chlorodiacetylbis(diphenylmethylphosphine)diplatinum:

m.pt. 151-153°C (decomp.). (Found: C 37.75, H 3.30% Calculated for $C_{30}H_{32}Cl_2O_2P_2Pt_2$: C 38.01, H 3.41%)

Di-μ-chlorodibenzoylbis(triethylphosphine)diplatinum:

m.pt. 153°C. (Found: C 34.37, H 4.38% Calculated for $C_{26}H_{40}Cl_2O_2P_2Pt_2$: C 34.40, H 4.45%)

Di-μ-chlorodibenzoylbis(dimethylphenylphosphine)diplatinum:

m.pt. 166-168°C (decomp.). (Found: C 37.89, H 3.28% Calculated for $C_{30}H_{32}Cl_2O_2P_2Pt_2$: C 38.01, H 3.41%)

Di-μ-chlorodibenzoylbis(triphenylphosphine)diplatinum:

m.pt. 287-291°C (decomp.). (Found: C 50.23, H 3.25% Calculated for $C_{50}H_{40}Cl_2O_2P_2Pt_2$: C 50.21, H 3.37%)

Di-μ-bromodibenzoylbis(diphenylmethylphosphine)diplatinum:

$[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ (0.304g, 0.52 mmol) was stirred with lithium bromide (ca 1.0g, 11.5 mmol) in acetone (50cm^3) under nitrogen for 18 h, then heated briefly to 50°C. The solvent was removed and the oily residue was treated with a 4:1 chloroform/water mixture. The chloroform layer was withdrawn, dried over anhydrous $MgSO_4$, and filtered. Addition of diethyl ether caused precipitation of colourless crystals of $[Pt_2(\mu\text{-}Br)_2(COPh)_2(PMePh_2)_2]$, m.pt. 165-170°C (decomp.). (Found: C 41.23, H 3.33% Calculated for $C_{40}H_{36}Br_2O_2P_2Pt_2$: C 41.38, H 3.13%)

Di-μ-iododibenzoylbis(diphenylmethylphosphine)diplatinum:

Treatment of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ with lithium iodide, in a manner analogous to that described above, gave yellow crystals of $[Pt_2(\mu\text{-}I)_2(COPh)_2(PMePh_2)_2]$, m.pt. 243-244°C. (Found: C 38.16, H 2.90, I 20.1% Calculated for $C_{40}H_{36}I_2O_2P_2Pt_2$: C 38.28, H 2.89, I 20.3%)

Similarly, treatment of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ with sodium benzylthiolate produced $[Pt_2(\mu\text{-}SCH_2Ph)_2(COPh)_2(PMePh_2)_2]$, but this complex was not isolated in a pure form.

cis-Dichloro(carbonyl)tricyclohexylphosphineplatinum:

Carbon monoxide was passed through a suspension of $[PtCl_2(norborna-diene)]$ (0.256g, 0.72 mmol) in chloroform ($40cm^3$). After 2 h PCy_3 (0.200g, 0.71 mmol) was added. A further 1 h later the solvent was removed, the residue was stirred with charcoal in benzene, and the solution was filtered. Addition of pet. ether (b.p. 40-60°) caused precipitation of a white solid (0.125g, 31%), which was recrystallised from $CHCl_3/Et_2O$ to give colourless crystals of cis-$[PtCl_2(CO)(PCy_3)]$, ν(CO) 2099 cm^{-1} in $CHCl_3$ solution. (Found: C 39.66, H 5.93% Calculated for $C_{19}H_{33}Cl_2OPPt$: C 39.72, H 5.80%)

cis-Dichloro(carbonyl)tri-o-tolylphosphineplatinum:

This complex was prepared similarly, ν(CO) 2110 cm^{-1} in $CHCl_3$ solution. (Found: C 44.21, H 3.65% Calculated for $C_{22}H_{21}Cl_2OPPt$: C 44.15, H 3.54%)

The complex cis-$[PtCl_2(CO)(PCy_3)]$ was also prepared by passing carbon monoxide through a solution of trans-$[PtCl_2(PCy_3)_2]$ (0.5g) in sym-tetrachloroethane ($50cm^3$) at 75°C for 32 h, the resultant oil after solvent removal being crystallised from CH_2Cl_2/Et_2O to give the product as colourless crystals.

Di-μ-chlorodibenzoylbis(tricyclohexylphosphine)diplatinum:

This complex was prepared in a manner similar to that of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, the infrared spectrum of the colourless, crystalline material produced having ν(CO) at 2065 and 1635 cm^{-1}. (Found: C 48.66, H6.21% Calculated for $C_{50}H_{76}Cl_2O_2P_2Pt_2$: C 48.74, H 6.22%)

Chloro(phenyl)carbonyl(tri-o-tolylphosphine)platinum:

cis-$[PtCl_2(CO)\{P(o\text{-tolyl})_3\}]$ (65.7mg, 0.11 mmol) and $HgPh_2$ (39.0mg, 0.11 mmol) were stirred together in benzene ($5cm^3$) under nitrogen for 8 h. Phenylmercuric chloride was filtered off, and addition of pet. ether (b.p. 40-60°) caused precipitation of colourless crystals of $[PtClPh(CO)\{P(o\text{-tolyl})_3\}]$, m.pt. 171-172°C. (Found: C 52.50, H 4.45% Calculated for $C_{28}H_{26}ClOPPt$: C 52.54, H 4.10%)

Benzyl(chloro)carbonyl(diphenylmethylphosphine)platinum:
cis-$[PtCl_2(CO)(PMePh_2)]$ (0.52g, 1.06 mmol) and dibenzylmercury (0.406g, 1.06 mmol) were stirred in benzene ($60cm^3$) at 45°C, under a CO atmosphere, for 48 h. The solvent was removed and the residue was treated with benzene ($8cm^3$) and n-pentane ($40cm^3$), causing deposition of a grey solid. This was filtered off and colourless crystals precipitated from the filtrate. The crystals were removed and treated at 70°C/0.005 torr. A little benzylmercuric chloride sublimed out, leaving $[PtCl(CH_2Ph)(CO)(PMePh_2)]$ as a near-colourless solid, m.pt. 106-109°C. (Found: C 45.81, H 3.83% Calculated for $C_{21}H_{20}ClOPPt$: C 45.86, H 3.67%)

trans-Benzoyl(chloro)bis(diphenylmethylphosphine)platinum:
$[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$ (0.127g, 0.119 mmol) was dissolved in methylene chloride ($20cm^3$) under nitrogen, and $PMePh_2$ (44.1µl, 0.238 mmol) was added. The solution was stirred for 4 h, the solvent was removed, and the residue was crystallised from CH_2Cl_2/Et_2O to give trans-$[PtCl(COPh)(PMePh_2)_2]$ as pale yellow crystals, m.pt. 165°C. (Found: C 53.90, H 4.67% Calculated for $C_{33}H_{31}ClOP_2Pt$: C 53.84, H 4.25%)

Similarly, addition of 1 mol equiv of $PMePh_2$ to solutions of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMePh_2)_2]$ or $[Pt_2(\mu\text{-}Cl)_2(COMe)_2(PMePh_2)_2]$ caused formation of the corresponding trans-$[PtCl(COR)(PMePh_2)_2]$ complexes.

trans-Chloro(phenacetyl)bis(diphenylmethylphosphine)platinum:
$[PtCl(CH_2Ph)(CO)(PMePh_2)]$ (53.2mg, 0.097 mmol) was dissolved in benzene ($5cm^3$) under nitrogen. A solution of $PMePh_2$ (17.9µl, 0.097 mmol) in benzene ($5cm^3$) was prepared under nitrogen, and was added dropwise to the former solution over a period of 4 h. The solution was filtered and pet. ether (b.p. 40-60°) was added, causing precipitation of trans-$[PtCl(COCH_2Ph)(PMePh_2)_2]$ as colourless crystals, m.pt. 158-159°C. (Found: C 54.42, H 4.02% Calculated for $C_{34}H_{33}ClOP_2Pt$: C 54.44, H 4.44%)

trans-Benzoyl(chloro)bis(diphenylmethylarsine)platinum:

cis-$[PtCl_2(CO)(AsMePh_2)]$ (0.115g, 0.21 mmol) was suspended in benzene ($10cm^3$) under nitrogen. Diphenylmercury (0.076g, 0.21 mmol) was added, and the mixture was stirred for 2 h. A small amount of charcoal was introduced to the brown suspension, and stirring was continued for 15 min. To the pale yellow solution after filtration was added, over 2 h, a solution of $AsMePh_2$ (41μl, 0.21 mmol) in benzene ($2cm^3$). The solution was filtered, and the addition of pet. ether (b.p. 40-60°) caused precipitation of colourless crystals of trans-$[PtCl(COPh)(AsMePh_2)_2]$, m.pt. 163-165°C. (Found: C 48.05, H 3.94% Calculated for $C_{33}H_{31}As_2ClOPt$: C 48.09, H 3.79%)

trans-Benzoyl(chloro)bis(triphenylarsine)platinum:

This complex was prepared analogously, m.pt. 243-245°C. (Found: C 54.41, H 3.78% Calculated for $C_{43}H_{35}As_2ClOPt$: C 54.46, H 3.72%)

Treatment of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PCy_3)_2]$ with PCy_3.

When 2 mol equiv of PCy_3 was added to a $CHCl_3$ solution of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PCy_3)_2]$, the solution ir. spectrum showed no reaction to have occurred after 3 days, the ν(CO) bands observed at 2072 and 1627 cm^{-1} being those associated with the starting complex.

A similar result was obtained when 1 mol equiv of P(o-tolyl)$_3$ was added to a $CHCl_3$ solution of $[PtClPh(CO)\{P(o\text{-tolyl})_3\}]$, the ν(CO) band at 2083 cm^{-1} being due to the starting material.

Reaction between cis-$[PtCl_2(CO)(PMePh_2)]$ and $Hg(CCl{=}CCl_2)_2$.

To a solution of cis-$[PtCl_2(CO)(PMePh_2)]$ (0.178g, 0.36 mmol) in benzene ($30cm^3$) was added $Hg(CCl{=}CCl_2)_2$ (0.165g, 0.36 mmol) under nitrogen. After stirring at 50°C for 20 h the solution ir. spectrum showed a strong ν(CO) band at 2095 cm^{-1} in addition to the band due to cis-$[PtCl_2(CO)(PMePh_2)]$. The volume of the solution was reduced to $5cm^3$ and pet. ether (b.p. 40-60°) was added, causing precipitation of colourless crystals which were identified from their ir. spectrum

as cis-$[PtCl_2(CO)(PMePh_2)]$. The solvent was removed from the remaining solution and the resultant oil was treated with boiling pet. ether ($20cm^3$). On cooling were precipitated colourless crystals of $[PtCl(CCl{=}CCl_2)(CO)(PMePh_2)]$ (48.3mg, 23%), ν(CO) 2102 cm^{-1}. (Found: C 33.32, H 2.71% Calculated for $C_{16}H_{13}Cl_4OPPt$: C 32.61, H 2.23%)

Reactions in chloroform solution of cis-$[PtCl_2(CO)(PMePh_2)]$ with equimolar amounts of $Hg(CH_2Cl)_2$, $Hg(CH_2OMe)_2$, $Hg(C{\equiv}CMe)_2$, $Hg(C{\equiv}CPh)_2$, and Hg(azobenzene)$_2$ all showed partial reaction, but no platinum-containing species other than cis-$[PtCl_2(CO)(PMePh_2)]$ could be isolated in any case. Treatment of cis-$[PtCl_2(CO)(PMePh_2)]$ with $Hg(CH{=}CH_2)_2$ resulted in a brown suspension, whose ^{31}P n.m.r. and ir. spectra showed no reaction of the platinum complex to have taken place.

Di-μ-chlorodiphenylbis(diphenylmethylphosphine)diplatinum: $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ (2.13g, 2.29 mmol) was suspended in benzene ($120cm^3$) under nitrogen, and $HgPh_2$ (1.62g, 4.56 mmol) was added. The suspension was stirred for $4\frac{1}{2}$ h after which PhHgCl (1.07g) was filtered off. The volume of the solution was reduced causing further PhHgCl precipitation. This was removed by filtration and the remaining solvent was evaporated. The residue was crystallised from CH_2Cl_2/Et_2O to give $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ as colourless crystals (1.33g, 57%), m.pt. 239-240°C. (Found: C 45.02, H 3.43% Calculated for $C_{38}H_{36}Cl_2P_2Pt_2$: C 44.93, H 3.57%)

The following complexes were prepared similarly.

Di-μ-chlorodiphenylbis(triphenylphosphine)diplatinum: m.pt. 285-290°C (decomp.). (Found: C 50.09, H 3.67% Calculated for $C_{48}H_{40}Cl_2P_2Pt_2$: C 50.57, H 3.54%)

Di-μ-bromodiphenylbis(dimethylphenylphosphine)diplatinum: m.pt. 214-216°C. (Found: C 34.38, H 3.22% Calculated for $C_{28}H_{32}Br_2P_2Pt_2$: C 34.29, H 3.29%)

Di-μ-iododiphenylbis(diphenylmethylphosphine)diplatinum: $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (0.138g, 0.136 mmol) was stirred with finely powdered lithium iodide (0.93g, 6.94 mmol) in acetone for 20 h. The solution was then briefly heated, the solvent was removed, and the residue was treated with a 1:3 chloroform/water mixture. The chloroform layer was removed, dried over anhydrous $MgSO_4$ and filtered. Ether addition caused precipitation of near-colourless crystals of $[Pt_2(\mu\text{-}I)_2Ph_2(PMePh_2)_2]$ (84.3mg, 52%), m.pt. 246-248°C. (Found: C 37.92, H 3.00% Calculated for $C_{38}H_{36}I_2P_2Pt_2$: C 38.06, H 3.03%)

Di-μ-chlorodiphenylbis(triethylphosphine)diplatinum and di-μ-chlorodiphenylbis(dimethylphenylphosphine)diplatinum were also prepared by treatment with $HgPh_2$ of benzene solutions of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ and $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$, respectively, but the complexes were not isolated in an analytically pure form.

Treatment of $[Pt_2(\mu\text{-}Br)_2Br_2(PMe_2Ph)_2]$ with 2 mol equiv of $Hg(CH_2Ph)_2$ in benzene solution resulted in formation of a dark solution and considerable black deposits, from which no solid material could be extracted.

Addition of $HgEt_2$ (0.05cm^3, 0.47 mmol) to a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ (0.22g, 0.24 mmol) in benzene (30cm^3) under nitrogen. After solvent removal and treatment with benzene/hexane were isolated a few colourless crystals, which were identified as trans-$[PtClEt(PMePh_2)_2]$, $^1J(Pt\text{-}P)$ 3235 Hz.

trans-Chloro(phenyl)bis(diphenylmethylphosphine)platinum: cis-$[PtCl_2(PMePh_2)_2]$ (0.377g, 0.566 mmol) and $HgPh_2$ (0.201g, 0.566 mmol) were refluxed in ethanol (50cm^3) under nitrogen for 24 h. The solvent was removed and the residue was treated at 90°C/0.001 torr for 12 h. Phenylmercuric chloride (0.146g, 85%) was thus obtained by sublimation, and the residue was crystallised from benzene/

pet. ether (b.p. 40-60°) to give trans-$[PtClPh(PMePh_2)_2]$ as colourless crystals, m.pt. 185°C. (Found: C 54.41, H 4.31% Calc'd for $C_{32}H_{31}ClP_2Pt$: C 54.28, H 4.42%)

Reaction between cis-$[PtCl_2(CO)(PMePh_2)]$ and phenyl-lithium.

To a solution of cis-$[PtCl_2(CO)(PMePh_2)]$ (0.336g, 0.68 mmol) in dry benzene ($30cm^3$) was added a benzene/ether solution of phenyl-lithium (0.72 mmol) over $1\frac{1}{2}$ h, under an atmosphere of carbon monoxide. The solution became dark brown, and after 2 h the solution infrared spectrum showed several bands in the 2000-2200 cm^{-1} region. After several crystallisation attempts, an ether extract of the residue was passed down a short chromatographic column (Florisil), but no pure material could be isolated.

In similar reactions, the solvents were removed and the ^{31}P n.m.r. spectrum of the residue, dissolved in $CDCl_3$, recorded. This was complex, showing the presence of $[PtClPh(CO)(PMePh_2)]$ (isomer II), trans-$[PtClPh(PMePh_2)_2]$, and trans-$[PtCl(COPh)(PMePh_2)_2]$, as well as other unidentified products (δP 5.7 p.p.m., ^1J 2953 Hz and δP 2.4 p.p.m., ^1J 1602 Hz).

Chloro(phenyl)carbonyl(diphenylmethylphosphine)platinum(II and III): $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (0.177g, 0.175 mmol) was dissolved in CH_2Cl_2 ($30cm^3$) and carbon monoxide was passed through the solution for 2 h. The solvent was removed without heating to leave a pale brown solid. This was dissolved in benzene ($5cm^3$), through which CO was passed for 1 min, and then filtered. Addition of pet. ether (b.p. 40-60°) caused precipitation of $[PtClPh(CO)(PMePh_2)]$ as colourless crystals. These were treated at 70-80°C/0.15 torr for 2 h to drive off residual benzene. (Found: C 44.99, H 3.33% Calc'd for $C_{20}H_{18}ClOPPt$: C 44.82, H 3.39%)

Treatment with carbon monoxide of benzene solutions of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PEt_3)_2]$, $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMe_2Ph)_2]$ or $[Pt_2(\mu\text{-}Br)_2Ph_2(PMe_2Ph)_2]$

produced strong ν(CO) bands in the solution ir. spectrum in each case. Total loss of carbon monoxide occurred on attempted isolation in each case, although the carbonylplatinum species were stable in solution at room temperature for several days. A similar ir. spectrum was produced when carbon monoxide was passed through a chloroform solution of $[Pt_2(\mu\text{-}I)_2Ph_2(PMePh_2)_2]$, but gradual loss of carbon monoxide occurred on standing for 2 days.

Reaction between $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$ and carbon monoxide.

Carbon monoxide was passed through a suspension of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$ (98.0mg, 0.086 mmol) in chloroform (20cm^3). No insoluble material remained after 2 h, and the solution ir. spectrum showed a strong absorption at ca 2110 cm^{-1}. The solvent was removed and the residue was crystallised from benzene/pet. ether (b.p. 40-60°) over ca 24 h. The ir. spectrum of the resultant crystalline solid showed it to be a mixture, the presence of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PPh_3)_2]$ being indicated by a band at 1645 cm^{-1} (by comparison with a genuine sample). The other component of the mixture exhibited a strong ν(CO) band at 2110 cm^{-1}, and was taken to be $[PtClPh(CO)(PPh_3)]$ (II and III).

Reactions of $[PtClPh(CO)(PMePh_2)]$.

1. Addition of $PMePh_2$.

Dropwise addition of 1 mol equiv of $PMePh_2$ in $CDCl_3$ to a solution of $[PtClPh(CO)(PMePh_2)]$ over ca 1 h resulted in almost complete loss of the carbonyl absorption in the solution ir. spectrum. A very weak band at 1620 cm^{-1}, indicative of an aroylplatinum derivative, was observed, however. After solvent removal, the ir. spectrum indicated the main product to be trans-$[PtClPh(PMePh_2)_2]$, by comparison with the spectrum of an authentic sample.

2. Heating in $CDCl_3$ solution.

When a 0.01M solution of $[PtClPh(CO)(PMePh_2)]$ was heated to 50°C for 2 h the solution ir. spectrum showed almost total loss of

the carbonyl absorption at ca 2100 cm^{-1}. The ir. spectrum of the solid residue after solvent removal showed a weak aroyl band at 1638 cm^{-1}, but the main product was identified as $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ by comparison with the ir. spectrum of an authentic sample.

3. Standing at ambient temperature in $CDCl_3$ solution.

A solution of $[PtClPh(CO)(PMePh_2)]$ was allowed to stand in air at ambient temperature for 7 days. After this time the ^{31}P n.m.r. spectrum showed the presence of small amounts of $[PtClPh(CO)(PMePh_2)]$ (isomer I) and $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PMePh_2)_2]$, although the main components of the mixture were still $[PtClPh(CO)(PMePh_2)]$ (isomers II and III).

4. Subjection to a stream of nitrogen.

A solution of $[PtClPh(CO)(PMePh_2)]$ in sym-tetrachloroethane was prepared by passing carbon monoxide through a solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$. The solution was halved, nitrogen gas being passed through one fraction while the other was allowed to stand untreated. Solution ir. spectra, recorded after 7 and 21 h, showed ca 50% loss of CO in the former case relative to the latter.

5. Addition of chlorine gas.

Chlorine gas was bubbled through a chloroform solution of $[PtClPh(CO)(PMePh_2)]$ for 10 min. The ir. spectrum of the intense yellow-green solution showed that total loss of CO had occurred. The solvent was removed, and the residue was crystallised from benzene/pet. ether (b.p. 40-60°) to give yellow crystals of $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$, m.pt. 120-121°C. (Found: C 38.88, H 3.29, Cl 18.72% Calculated for $C_{38}H_{36}Cl_6P_2Pt_2$: C 39.41, H 3.14, Cl 18.38%)

The complex $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$ was also prepared by passing chlorine gas through a CH_2Cl_2 solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$.

Reaction between $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$ and carbon monoxide.

Carbon monoxide was passed through a chloroform solution of $[Pt_2(\mu\text{-}Cl)_2Cl_4Ph_2(PMePh_2)_2]$ for 4 h. The solution ir. spectrum showed a strong absorption at 2115 cm^{-1}. The solvent was removed, and the residue was crystallised from benzene/pet. ether (b.p. 40-60°) to yield colourless crystals of cis-$[PtCl_2(CO)(PMePh_2)]$, identified by comparison of the ir. spectrum with that of a genuine sample.

Chloro(phenyl)(1,5-cyclooctadiene)platinum:

$[PtCl_2(cod)]$ (4.89g, 13.1 mmol) was added to a solution of $HgPh_2$ (4.64g, 13.1 mmol) in CH_2Cl_2 (100cm^3) under nitrogen. After stirring for 21 h, PhHgCl (3.32g, 81%) was filtered off. The solvent was removed, and the residue was treated at 90°C/0.001 torr for 8 h to remove final traces of PhHgCl. The greyish solid which remained was treated with CH_2Cl_2/Et_2O, giving masses of white crystals of [PtClPh(cod)] (3.39g, 65%), m.pt. 165-167°C (lit.value 166-168°C[71]).

trans-Chloro(phenyl)bis(tricyclohexylphosphine)platinum:

A solution of [PtClPh(cod)] (0.861g, 2.07 mmol) in CH_2Cl_2 (20cm^3) was prepared under nitrogen. Tricyclohexylphosphine, previously recrystallised from ethanol, (1.161g, 4.15 mmol) was added, and the solution was stirred for 4 h. The volume of the solution was reduced to 5cm^3, and the addition of n-pentane caused precipitation of white crystals of trans-$[PtClPh(PCy_3)_2]$ (1.256g, 70%), m.pt. 279-280°C. (Found: C 57.85, H 8.05% Calculated for $C_{42}H_{71}ClP_2Pt$: C 58.10, H 8.25%)

Reaction between trans-$[PtClPh(PCy_3)_2]$ and carbon monoxide.

In a 5cm^3 flask was prepared a solution of trans-$[PtClPh(PCy_3)_2]$ (74.2mg, 0.086 mmol) in sym-tetrachloroethane (1.5cm^3). The system was evacuated and let down to an atmosphere of carbon monoxide (56.5% C-13 labelled). The solution was heated to 70°C for 7 days. After this time, by ^{13}C and ^{31}P n.m.r. spectroscopy were identified

cis-$[PtCl_2(CO)(PCy_3)]$ and two isomers of $[PtClPh(CO)(PCy_3)]$. Neither that isomer with Ph trans to PCy_3 nor the aroylplatinum complex, $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PCy_3)_2]$, were observed. No attempt was made to isolate any product of this reaction owing to the complex nature of the reaction mixture.

CHAPTER FOUR

Isomerisation Reactions of Platinum Complexes

The role of 5- and 3-coordinate intermediates in isomerisation reactions of platinum(II) and palladium(II).

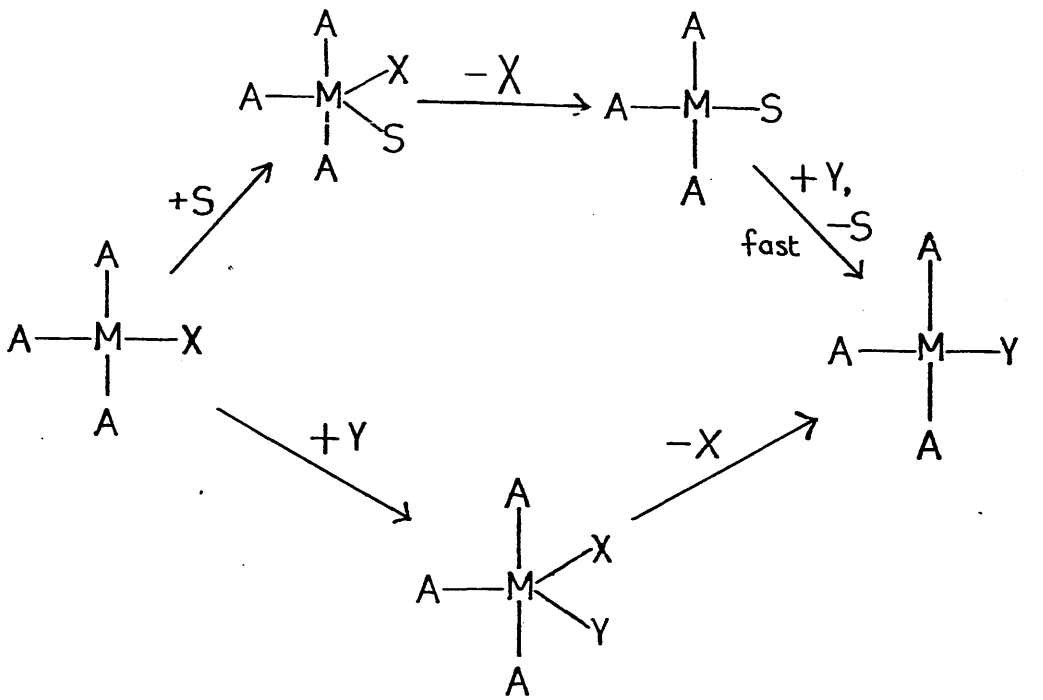
Substitution reactions of square-planar platinum(II) and palladium(II) complexes

$$MA_3X + Y \longrightarrow MA_3Y + X \qquad (M = Pd \text{ or } Pt)$$

occur with retention of configuration, and can be described by the general rate equation

$$\text{rate} = \{k_1 + k_2[Y]\}[MA_3X]$$

This indicates the existence of two parallel mechanisms, one of which is solvent-dependent, the other being believed to involve direct interaction of the complex with the incoming nucleophile.[45,97] Both routes are thought to be associative, involving trigonal bipyramidal intermediates:



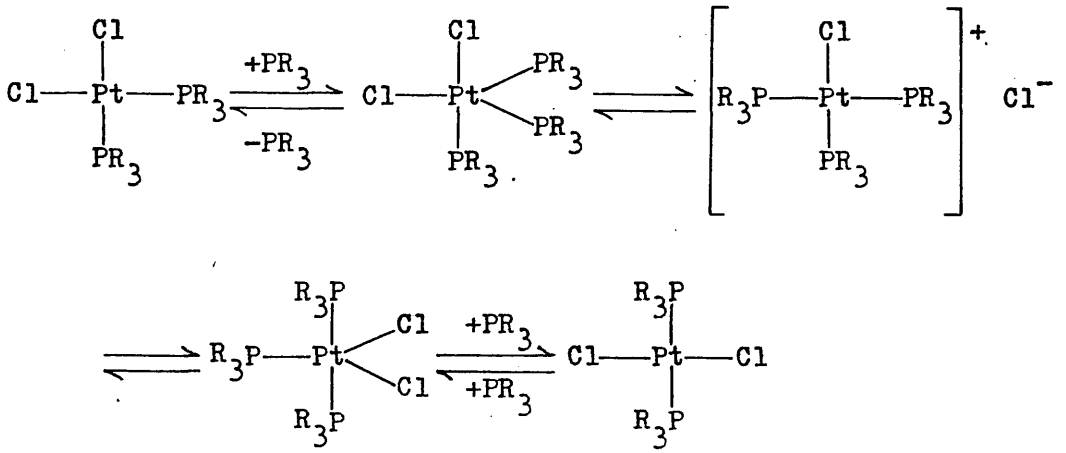
Isomerisation of square-planar platinum(II) and palladium(II) complexes, which is usually slow except in the presence of a catalyst, is apparently less simple and a number of isomerisation routes have been postulated. Isomerisation of cis- or trans-complexes in solution can be achieved by the addition of a nucleophile,[219] or photochemically,[220] while certain complexes undergo spontaneous isomerisation at or above ambient temperature.[101,221]

For the complexes $[PtX_2(ER_3)_2]$ (E = P, As or Sb), a thermodynamic study of cis-trans isomerisation in benzene solution was carried out.[219] This indicated that the trans-isomer is thermodynamically more stable in solution, due to the increase in entropy during its formation from the cis-isomer, the process involving release of the benzene molecules associated with the highly polar cis-complex. The cis-isomer was found to have a greater heat of formation, however, and this was thought to be due to its more favourable arrangement of ER_3 ligands with respect to π-overlap with the d-orbitals of the metal,[45,97] although it is now believed to be primarily due to the high trans-influence of ER_3.

In contrast, a study of the uncatalysed cis-trans isomerisation of the palladium(II) complexes, $[PdCl_2L_2]$ (L = PMe_2Ph or $PMePh_2$), showed[222] the cis-isomer to be thermodynamically more stable, but again it was pointed out that the isomerisation process was entropy-controlled.

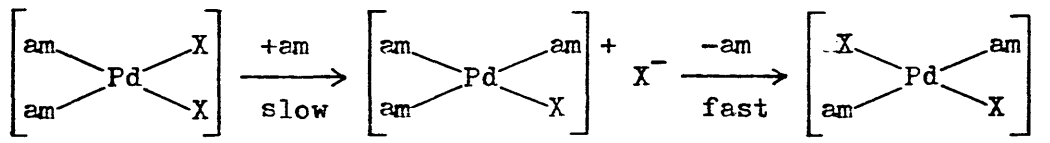
The most commonly encountered and generally accepted mechanism for cis-trans isomerisation was one of double displacement, which involved an ionic intermediate. For the interconversion of cis- and trans-$[PtX_2(PR_3)_2]$, two observations in particular favoured such a proposal. The fact that isomerisation was very slow unless a catalyst was added suggested the operation of an intermolecular process and, secondly, since substitution reactions occur with

retention of configuration at least two displacement steps would be necessary for isomerisation:



The complexes cis-$[PtClR(PEt_3)_2]$ (R = Me or Ph) were rapidly converted to their trans-isomers in solution when a trace of PEt_3 was added,[16a] but the complexes $[PtR_2(PEt_3)_2]$ could not be so isomerised. These observations also pointed to the involvement of an ionic intermediate, $[PtR(PEt_3)_3]^+ Cl^-$, in the process.[16b]

The cis-trans isomerisation of $[PdX_2(amine)_2]$ (X = N_3, Br, I or CNS) was found to be catalysed by free amine,[223] the rate showing a first order dependence on the concentrations of the complex and the amine, and displacement of the anionic ligand was proposed to be the rate-determining step:



The first indication that the double displacement mechanism for isomerisation might not be universally operative came from a study of the isomerisation of cis-$[PtCl_2(PBu^n_3)_2]$ in cyclohexane.[98] Isomerisation was immeasurably slow unless PBu^n_3 was added, and it was found that the rate was reduced by addition of a polar solvent.

The latter observation was in contrast to the effect of polar solvents on the rates of substitution reactions of platinum(II) compounds,[224] and suggested that a consecutive displacement mechanism was not involved. Formation of a five-coordinate species, thereby explaining the high ΔS^{*} barrier (-36.9 e.u.), which could undergo pseudorotation, was suggested as an alternative isomerisation mechanism.[98]

This proposal was modified by the same authors when they discovered that isomerisation of $[PtX_2L_2]$, in the presence of a catalytic amount of tertiary phosphine L' (where $L' \neq L$), produced no phosphine exchange during isomerisation.[225] They pointed out that if phosphine exchange was rapid compared to isomerisation, then identical rates of isomerisation of cis-$[PtX_2L_2]$ would be obtained for different L'. This was not found and, since no phosphine exchange was detected, it was concluded that isomerisation must proceed much faster than exchange.[225] They suggested that these observations were not compatible with a consecutive displacement mechanism or a straightforward pseudorotation, as either mechanism would involve interchange of L and L' at some point. It was concluded that a distorted five-coordinate species, in which L' occupies an unique position throughout, must be involved, and that this distorted state must be able to undergo some fluxional change which interconverts the positions of L and X.[225]

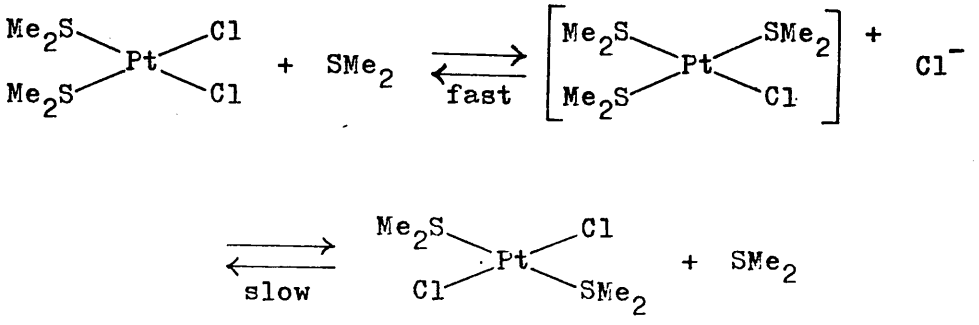
Haake and Pfeiffer also suggested that the unusual effect of polar solvents on the rates of such isomerisations could be explained by considering the nature of the species present in solution. They found[226] that, for most polar solvents, a complex containing one solvent molecule was present in solution (the exception being methanol, where two associated solvent molecules were detected). If dissociation of this molecule was required, as seemed likely, before

isomerisation could occur under the influence of the catalyst, reduction of the rate of isomerisation would follow.

Cooper and Powell subsequently studied the tertiary phosphine catalysis of cis-trans isomerisation and ligand exchange reactions of the complexes cis-$[PtX_2L_2]$ (X = Cl or I; L = tertiary phosphine).[99] They found that the thermodynamic stability of the mixed species $[PtX_2LL']$ relative to $[PtX_2L_2]$ or $[PtX_2L'_2]$ was dependent on L and L', and in certain cases the mixed complexes $[PtX_2LL']$ were considerably less stable. Thus, conclusions based[225] on the failure to find exchange of L and L' were invalid,[99] since the products of such exchange might be thermodynamically unstable. It was pointed out that such evidence did not disprove the operation of a pseudorotation mechanism, but it was also emphasised that such a mechanism for cis-trans isomerisation of platinum(II) complexes was unlikely, since stereochemical specificity in substitution reactions, due to the trans-effect, is a pronounced feature of their chemistry.[99]

The cis-trans isomerisation of the palladium(II) complexes $[PdCl_2(PMe_2R)_2]$ (R = o-tolyl or α-naphthyl) was shown to be catalysed by a variety of ligands L,[227] and n.m.r. and kinetic studies gave results which were suggested to be fully consistent with a consecutive displacement mechanism, involving ionic species of the type $[PdCl(PMe_2R)_2L]^+ Cl^-$ as intermediates.

Further strong evidence for the operation of a consecutive displacement mechanism was obtained from an investigation of the equilibrium energetics and kinetics of the cis-trans isomerisation of $[PtCl_2(SMe_2)_2]$.[228] In the presence of free dimethylsulphide, the rate was found to depend on the concentrations of the complex and the ligand. The $[PtCl(SMe_2)_3]^+$ cation was found as an isolable intermediate in the reaction, and this was taken to indicate the operation of a double displacement mechanism:



With the analogous palladium(II) complexes, however, addition of SMe_2 to trans-$[PdCl_2(SMe_2)_2]$ did not cause isomerisation, but a fast ligand exchange was observed.[228]

Further support for a fluxional five-coordinate intermediate was proffered when the results of a study of the cis-trans isomerisation of $[PtCl_2(PEt_3)_2]$ were published by Louw[229] in 1974. He found that the complex $[PtCl(PEt_3)_3]^+ ClO_4^-$ did not react with chloride ions to form either cis- or trans-$[PtCl_2(PEt_3)_2]$, although a fast reaction would be expected if the consecutive displacement mechanism was operative. Louw also observed that catalysis of the isomerisation by PPh_3, or addition of PEt_3 to a solution of cis-$[PtCl_2(PPh_3)_2]$, did not produce mixed phosphine complexes. He suggested that these data contradict the consecutive displacement mechanism for isomerisation, and favour one of fluxional rotation.

Later that year, Powell and Cooper showed that these data are, in fact, consistent with a consecutive displacement mechanism.[230] They pointed out that the equilibrium

$$[PtCl(PEt_3)_3]^+ + Cl^- \rightleftharpoons \text{cis-}[PtCl_2(PEt_3)_2] + PEt_3$$

lies well to the left-hand side in the $MeOH/CH_2Cl_2/n\text{-}C_6H_{14}$ solvent mixture used by Louw, and that it had previously been noted that the

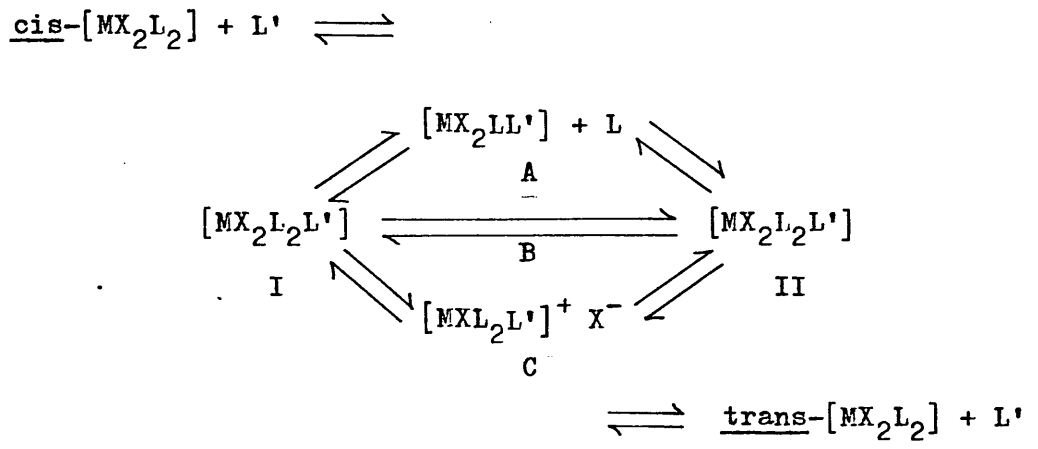
use of methanol as solvent stabilised ionic intermediates and inhibited isomerisation, possibly in part by solvation of the chloride ions.[99,225-227] Also, addition of PPh_3 to solutions of cis-$[PtCl_2(PEt_3)_2]$ resulted in detection of cis-$[PtCl_2(PEt_3)_2]$ and free PPh_3 only since, under these conditions, PPh_3-containing complexes are thermodynamically less stable than cis-$[PtCl_2(PEt_3)_2]$. It was also shown[230] that addition of 3.5 molar equivalents of PEt_3 to a suspension of the sparingly soluble cis-$[PtCl_2(PPh_3)_2]$ in chloroform produced the ionic complex $[PtCl(PEt_3)_3]^+ Cl^-$ in solution, since the equilibrium

$$\text{cis-}[PtCl_2(PPh_3)_2] + 3PEt_3 \rightleftharpoons [PtCl(PEt_3)_3]^+ Cl^- + 2PPh_3$$

lies well to the right. Addition of methanol, followed by cooling of the solution, allowed isolation of cis-$[PtCl_2(PPh_3)_2]$ due to its low solubility. Thus, for these systems, no mixed phosphine complexes would be isolated after attempting to isomerise $[PtCl_2L_2]$ by the addition of a different phosphine, L'. It was therefore stated[230] that the results presented by Louw were indeed fully consistent with a consecutive displacement mechanism.

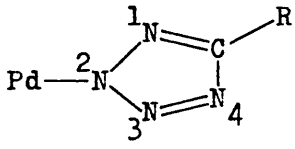
Evidence that a third isomerisation route could operate was presented by Redfield and Nelson. They showed[231] that mixing cis-$[MCl_2\{P(OMe)_3\}_2]$ with cis- and trans-$[MCl_2(PMePh_2)_2]$ (M = Pd or Pt) produced complexes of the type $[MCl_2\{P(OMe)_3\}(PMePh_2)]$, and that $P(OMe)_3$ catalysed isomerisation of cis-$[PtCl_2(PMePh_2)_2]$, the complex $[PtCl_2\{P(OMe)_3\}(PMePh_2)]$ again being formed. (Addition of PPh_3 to cis-$[PtCl_2(PMePh_2)_2]$, however, did not catalyse isomerisation and no mixed phosphine species were observed.) Conductometric titrations indicated the absence of any ionic species. Ligand mixing indicated that no unique M-L' bond was formed in a possible five-

coordinate intermediate and, since no ionic intermediates were detected, it was suggested that in this case the isomerisation mechanism involved consecutive neutral ligand displacement,[231] though such a process alone could not produce isomerisation. They concluded that there existed no unique isomerisation mechanism, but that any one of the three might operate under various conditions:



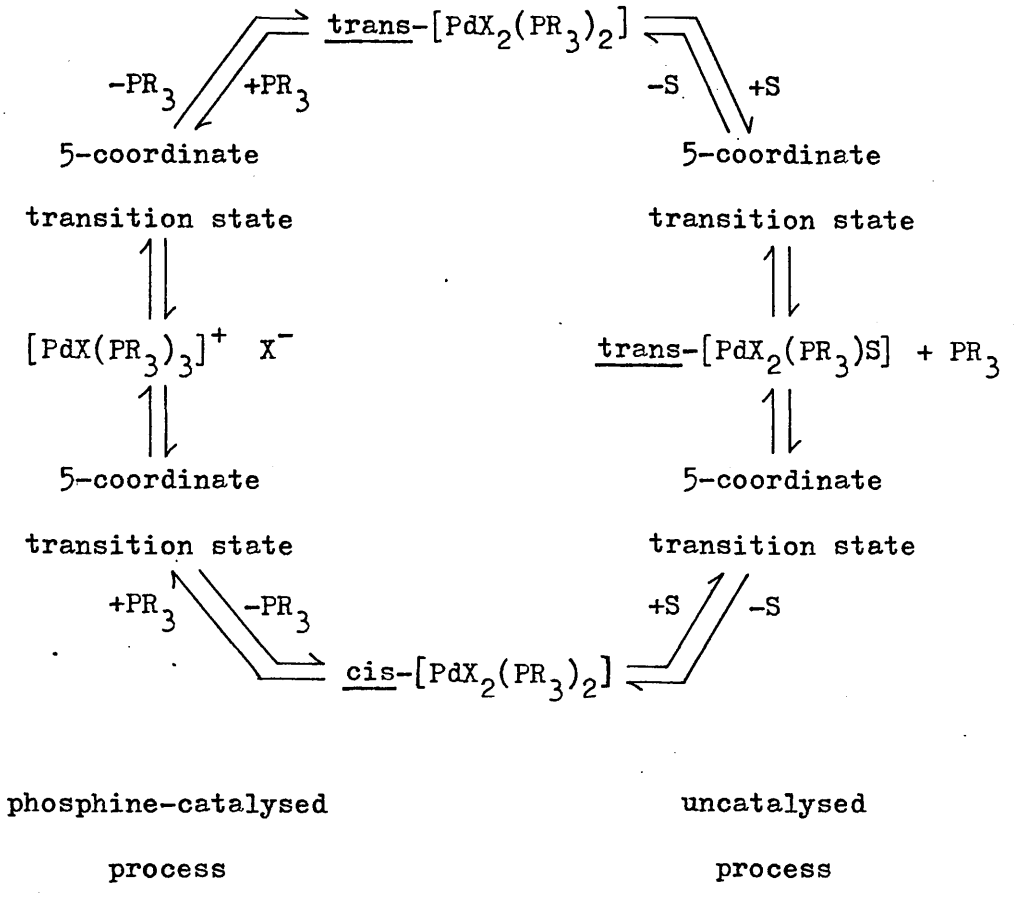
Pathway A is consecutive ligand displacement and would be favoured by non-polar solvents and where X^- is strongly coordinating; pathway B is fluxional rotation between the five-coordinate species I and II and would dominate in non-polar solvents when L and L' are small and of near-identical nucleophilicities; pathway C is consecutive anion displacement and would tend to operate in polar solvents, when X^- is poorly coordinating and L' is a good nucleophile.[231]

Since 1975 the relative importance and detailed operation of each of these three mechanisms have been frequently discussed, and the role of the solvent in isomerisation reactions has attracted increased attention. The mechanisms of catalysed and uncatalysed cis-trans isomerisation of $[Pd(PR_3)_2(tet)_2]$ (tet = 5-methyl- or 5-trifluoromethyltetrazolate) were investigated,[232] where the tetrazolate anion may be bonded to palladium via N_1 or N_2:



For mixtures of $[Pd(PMe_2Ph)_2(tet)_2]$ and $[Pd(PMePh_2)_2(tet)_2]$ the following behaviour was found. In the presence of free phosphine, tetrazolate exchange, as evidenced by the formation of both N_1- and N_2-bonded species, was faster than phosphine exchange, while in the absence of free phosphine, exchange of phosphine was the more rapid. The nature of the phosphine, tetrazolate and solvent were each found to affect the energetics of the process, the extent of ionic complex formation being dependent on the nucleophilicity of the catalytic agent. When no catalyst was added, the existence of ionic species was not detected. It was therefore suggested[232] that the transition states were fluxional five-coordinate species, the intermediates being four-coordinate where solvent had displaced phosphine or, in the presence of free phosphine, where anion displacement by the phosphine had taken place (Scheme 3). Since the rates of isomerisation depended on both coordinated and catalytic phosphine, the previously suggested[224] unique Pd-L' bond in the five-coordinate species was again considered unnecessary when $L \neq L'$.

These ideas of solvent- or ligand-associated intermediates were pursued in a study of cis-trans isomerisation reactions of the complexes $[PdX_2(PMe_{3-n}Ar_n)_2]$ (n = 1 or 2; Ar = p-$MeOC_6H_4$, p-MeC_6H_4, C_6H_5 or p-ClC_6H_4).[233] The effects of the halide, the solvent, and the electronic nature of the phosphine on the isomerisation process were considered, and the results for the uncatalysed reaction were believed to be consistent with the solvent-association mechanism outlined previously.[232] It may be noted that uncatalysed isomerisation



Scheme 3

reactions often involve solvent-associated species, and could more accurately be called "solvent-catalysed" reactions.

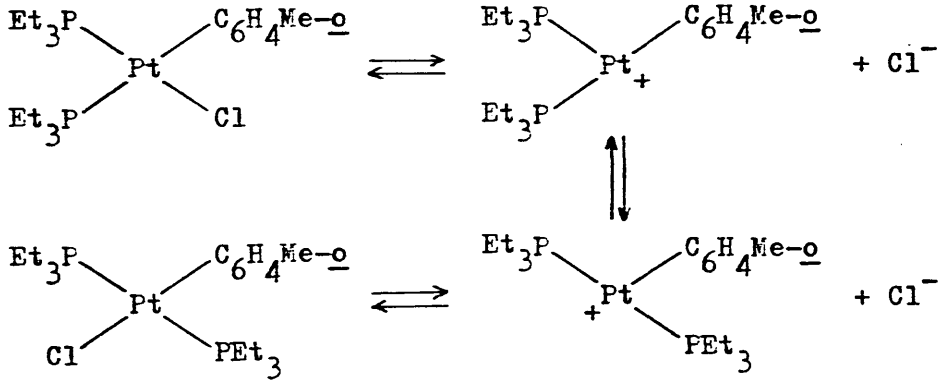
The above isomerisation mechanisms (Scheme 3) were also shown to be consistent with observations made on cis-trans isomerisation reactions of the complexes $[Pd(N_3)_2L_2]$ (L = PMe_2Ph or $PMePh_2$).[234] Investigations of the effects of added ligands indicated that five-coordinate species were formed, which dissociated only to ionic complexes, and that rapid isomerisation and/or ligand exchange took place. An ionic mechanism was considered unlikely since it was thought that X^- addition to $[PdXL_3]^+$ might be too slow to account for the fast isomerisation, as suggested by Louw.[229] The subsequent comments of Powell and Cooper,[230] however, refuted Louw's argument,

so a consecutive anion displacement mechanism might have provided a suitable explanation of the observations. The authors suggested, however, that solvent- or ligand-association to form five- and/or six-coordinate species, which could undergo fluxional rotation or ligand exchange, seemed the most likely mode of isomerisation.[234] They also concluded that isomerisation and substitution reaction mechanisms for square-planar palladium(II) complexes must be intimately related.

Fluxional five-coordinate intermediates were again featured when Louw showed that addition of L to the complexes $[PtX_2L_2]$ (X = Cl, Br or I; L = PEt_3 or PMe_2Ph) produced $[PtXL_3]^+ X^-$ in polar solvents, but $[PtX_2L_3]$ in non-polar media.[235] The five-coordinate species $[PtX_2(PMe_2Ph)_3]$ (X = Br or I) were isolated,[236] though their structures were not determined, but the crystal structure of $[PdCl_2(PMe_2Ph)_3]$ was shown to be intermediate between square pyramidal and trigonal bipyramidal in nature.[237] Louw therefore suggested that uncatalysed and iodide-catalysed isomerisations of $[PtX_2L_2]$ complexes occur *via* pseudorotation of a five-coordinate intermediate, and that the phosphine-catalysed reaction might also occur by this mechanism.[235] He also proposed that isomerisation of the complexes $[PtR_2L_2]$ (R = alkyl or aryl) could only satisfactorily be explained by invoking a pseudorotation mechanism, as might be the case for $[AuR_2R'L]$ systems. He did point out, however, that in the complexes $[PtXRL_2]$ the consecutive displacement mechanism becomes the dominant reaction pathway. Some doubt was cast on the last proposal, however, when it was shown that one of the basic rate laws used by Louw was incorrect and that he had apparently misinterpreted certain of the available data relevant to such reactions,[238] and it was claimed that there existed considerable evidence in favour of a dissociative route!

The idea that a dissociative process might operate in some of these reactions is perhaps the most revolutionary, and the first evidence that isomerisation of $[PtXRL_2]$ complexes might not occur by the accepted consecutive anion displacement mechanism was found by Romeo *et al*, from a kinetic study of the reaction of *trans*-$[PtClR(PEt_3)_2]$ (R = *o*-tolyl or mesityl) with various nucleophiles in methanol solution.[239] They found that chloride ion displacement did not occur in the classic manner, steric and electronic factors combining to prevent direct attack by the nucleophile, and the reaction rate was independent of the nature and concentration of the nucleophile.

Evidence for a dissociative isomerisation mechanism was obtained from a kinetic study of the uncatalysed conversion of *cis*-$[PtCl(o\text{-tolyl})(PEt_3)_2]$ into its *trans*-isomer.[101] This process exhibited mass-law retardation by chloride ions, while the substitution of chloride by iodide or cyanide obeyed the two-term rate law typical of substitution reactions of platinum(II) complexes. To explain these observations a non-synchronous mechanism was suggested,[101] in which the rate-determining step involves cleavage of the platinum-chlorine bond to yield a three-coordinate intermediate. It was further suggested that labile "*cis*-like" and "*trans*-like" three-coordinate species should be involved:



The authors pointed out that while such a dissociative path represents a negligible contribution to the reactivity in substitution reactions, as in the displacement of chloride by iodide or cyanide, it becomes the rate-determining process for [PtCl(o-tolyl)-$(PEt_3)_2$] isomerisation.[101]

Although three-coordinate platinum species represent 14-electron systems, which would be expected to be unstable according to Tolman's 16- and 18-electron rule,[37] such intermediates exist and have been postulated in several reaction sequences. These include the insertion of carbon monoxide into platinum-carbon bonds[192] (see also ch. 3), and decarbonylation,[194] olefin insertion into platinum-hydrogen bonds,[148,149] and the decomposition of cis-$[PtBu^n{}_2(PPh_3)_2]$.[118] A molecular orbital study of olefin insertion into the Pt-H bond has suggested that a dissociative reaction pathway in which the insertion step takes place at a four-coordinate species should be favoured, with T- or Y-shaped species being formed in preference to the symmetrical trigonal species.[146]

A series of studies was carried out on the substitution of chloride in the complexes $[PtClR(PEt_3)_2]$ in methanol solvent, and Romeo and coworkers suggested the involvement of a solvolytic pathway. The displacement of chloride by pyridine from trans-$[PtClR(PEt_3)_2]$ (R = phenyl, o-tolyl or mesityl) produced kinetic results consistent with the following reaction mechanism:[240]

$$\text{trans-}[PtClR(PEt_3)_2] + MeOH \underset{+Cl^-}{\overset{-Cl^-}{\rightleftharpoons}} \text{trans-}[PtR(PEt_3)_2(MeOH)]^+$$

$$\overset{+py}{\underset{-py}{\rightleftharpoons}} \text{trans-}[PtR(PEt_3)_2py]^+ + MeOH$$

Increasing bulk of the organic group caused a reduction in the

reaction rate, presumably due to increasing difficulty for the incoming group to approach the complex and form the transition state.[240] A further study of the reaction of *trans*-[PtCl(*o*-tolyl)-$(PEt_3)_2$] with various substituted pyridines suggested that the strong rate dependence on the incoming group arose from competition between chloride ion and pyridine for the reaction intermediate, and that the size and steric hindrance of the incoming substituted pyridine were of critical importance.[241]

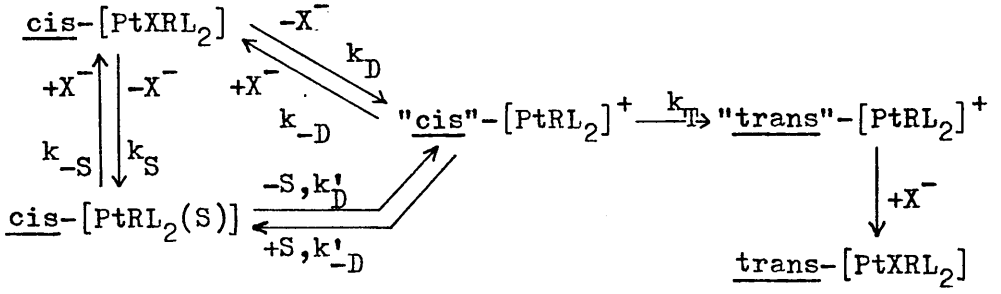
The same authors investigated[242] the effects of the bulk of the incoming nucleophile and of the organic group, R, on the rates of reaction of *trans*-$[PtXR(PEt_3)_2]^{n+}$ (R = phenyl, *o*-tolyl or mesityl) with substituted pyridine derivatives (X = MeOH, n = 1) or thiourea derivatives (X = Cl, n = 0). For the pyridine substitutions in particular, the reactions became slower as the steric hindrance increased. They suggested[242] that the ΔH^* and ΔS^* values obtained were consistent with an associative mechanism and formation of a five-coordinate transition state, but pointed out that, until the rate of MeOH exchange was known, a dissociative route could not be ruled out.

That isomerisation may be a complicating feature in substitution reactions was shown for chloride displacement from *cis*- and *trans*-$[PtClR(PEt_3)_2]$ (R = phenyl, *o*-tolyl or mesityl) by cyanide or pyridine.[243] The reactions of the *cis*-complexes with pyridine were slower and, since the rates of pyridine substitution were close to those of spontaneous isomerisation to the *trans*-form, it was suggested[243] that isomerisation of the *cis*-complexes, presumably *via* a dissociative route, takes place before or during the reaction with pyridine, the latter occurring by an associative solvent-assisted route.[240]

The role of three-coordinate intermediates, and the factors

which determine the dissociative or associative nature of reaction mechanisms, were again highlighted by Romeo in the mid-1970's. Steric hindrance by the organic group, R, caused a reduction in the rate of substitution of bromide in $[PtBrR(PEt_3)_2]$ complexes by methanol, while the isomerisation rate was largely unaffected.[244] These observations suggested that two different mechanisms were operative, and that the dissociative isomerisation route involved little steric relaxation in the intermediate. The electronic interaction between the metal and the aryl group was suggested to be important, but its exact nature had not yet been elucidated.[244]

Further information on the mechanisms of methanol solvolysis and isomerisation was obtained for the complexes cis-$[PtBrR(PEt_3)_2]$ (R = C_6H_5, p-MeC_6H_4, o-MeC_6H_4, o-EtC_6H_4 or 2,4,6-$Me_3C_6H_2$).[245] The authors postulated an associative mode of activation for solvolysis, but suggested that isomerisation proceeded via an asynchronous, dissociative mechanism for which the rate-determining step involved breaking of the Pt-Br bond to yield a "cis-like", three-coordinate intermediate:



The involvement of such intermediates in uncatalysed cis-trans isomerisation and ethylene insertion reactions has been discussed.[246]

Finally, further support for dissociative mechanisms for isomerisation has recently been claimed from studies of the isomerisation reactions of trans-$[PtCl_2L_2]$ (L = dialkylsulphoxide).[100]

Two possible mechanisms for the thermal trans→cis isomerisation were proposed, which could accomodate the observed kinetic data. Both involved displacement of a sulphoxide ligand by the chloroform solvent, and one mechanism would involve trans→cis isomerisation of the complex $[PtCl_2L(S)]$. The pathway favoured by the authors, however, involved solvent dissociation to yield a three-coordinate species which retained its stereochemical integrity:[100]

$$\underline{trans}\text{-}[PtCl_2L_2] + S \rightleftharpoons \underline{trans}\text{-}[PtCl_2L(S)] + L$$

$$\underline{trans}\text{-}[PtCl_2L(S)] \rightleftharpoons [PtCl_2L] + S$$

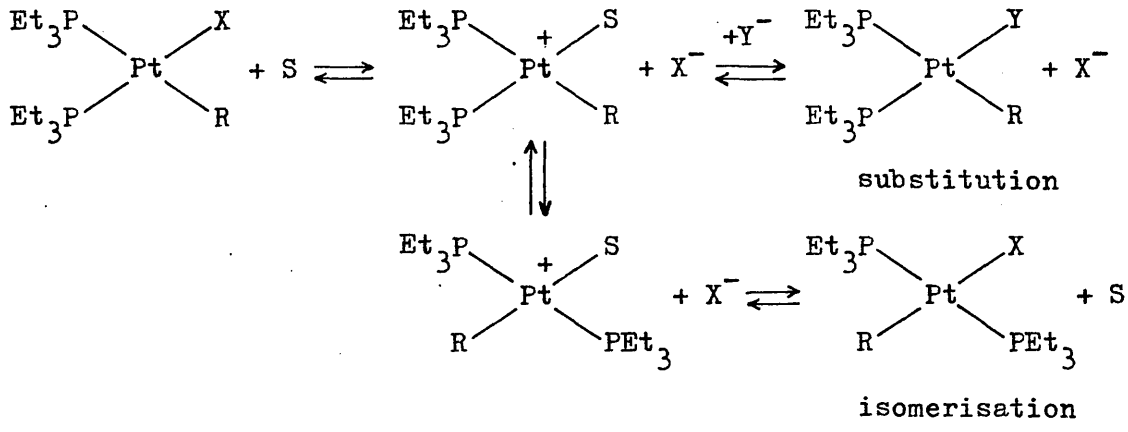
$$[PtCl_2L] + S \rightleftharpoons \underline{cis}\text{-}[PtCl_2L(S)]$$

$$\underline{cis}\text{-}[PtCl_2L(S)] + L \rightleftharpoons \underline{cis}\text{-}[PtCl_2L_2] + S$$

Geometric isomerisation of the three-coordinate intermediates was considered to be rapid, and they would probably be "cis-like" and "trans-like" species similar to those proposed by Romeo.[100]

Evidence for the intermediacy of three-coordinate species is not clear-cut, however, and it has recently been shown that many of the observations reported by Romeo et al on the cis-trans isomerisation and substitution reactions of the $[PtXR(PEt_3)_2]$ complexes can equally well be interpreted in terms of a solvent-association mechanism.[247] The authors pointed out that the rate law obtained for halide dissociation was identical to that found for halide displacement by the solvent (Scheme 4). It was suggested that the strongly negative ΔS^* values were indicative of an associative process, and that the ΔV^* values also reflected the operation of such a process. With the exception of R = mesityl, that is, for the less sterically hindered complexes, the solvolysis step was so rapid

that it could be considered as a pre-equilibrium step in the isomerisation process, and the measured rate would be the rate of



Scheme 4

isomerisation of $[PtR(PEt_3)_2(S)]^+$. For $[PtX(2,4,6\text{-}Me_3C_6H_2)(PEt_3)_2]$, however, the rate-determining step would be solvolysis, and it was suggested that the increased bulk with R = mesityl was more likely to inhibit solvent approach to the complex, rather than affect the rate of cleavage of the platinum-halide bond.[247] The authors therefore concluded that the isomerisation of cis-$[PtBr(2,4,6\text{-}Me_3C_6H_2)(PEt_3)_2]$ and the substitution reactions of cis- and trans-$[PtBr(2,4,6\text{-}Me_3C_6H_2)(PEt_3)_2]$ all proceed via an associative type of mechanism.

The main point to emerge from the preceding discussion is that many features of the isomerisation reactions of square-planar complexes of platinum(II) and palladium(II) are not well understood. As pointed out by Redfield, Cary and Nelson[233] it is likely that they are intimately related to substitution reactions of the same complexes, and it appears that the latter are not as easily described as was once thought.

Evidence has been presented to support a number of isomerisation

reaction pathways, and the operation of a particular mechanism may be critically dependent on the conditions under which the reaction is carried out, as emphasised by Redfield and Nelson.[231] The consecutive anion displacement route, which for a considerable time was believed to be universally operative, is perhaps the best documented, and several attempts to disprove its involvement in certain cases have been unsuccessful. A variation of this mechanism, which has not really been investigated, is that of ion pair formation, and it may be that such species are also involved in some cases.

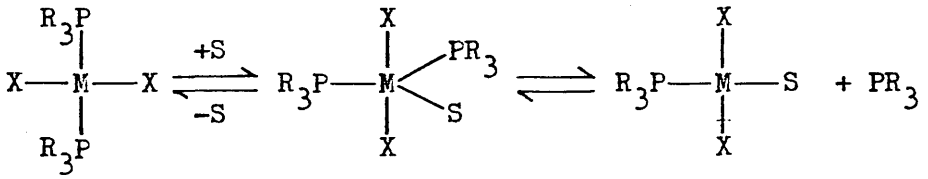
Consecutive neutral ligand displacement, where a catalyst displaces a previously coordinated ligand, has been shown to operate in at least one case, but such a process has not been shown to be widespread, and it is not clear how this can effect isomerisation. Displacement of L from $[PtX_2L_2]$ by L', for example, would produce $[PtX_2LL']$ of the same geometry; re-attack of L, with subsequent displacement of L', would simply regenerate the initial complex. This process, however, may operate in conjunction with another reaction pathway to effect isomerisation.

The operation of fluxional rotation or pseudorotation mechanisms involving five-coordinate intermediates has not been disproved but, in general, it has not been found necessary to invoke such processes, and they are not easy to reconcile with the operation of the trans-effect, which is well-established for platinum(II) complexes in particular. In certain cases, however, such as the cis-trans isomerisation of $[AuMe_2R(PPh_3)]$,[248] where X^- elimination is not possible, a pseudorotation mechanism involving $[AuMe_2R(PPh_3)_2]$ species remains an attractive possibility, although PPh_3 dissociation could also occur. The complexes cis- and trans-$[PtR_2(PEt_3)_2]$ (R = Me or Ph) were found to resist isomerisation, however.[16b]

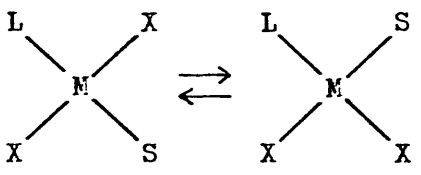
Dissociative mechanisms involving three-coordinate intermediates

are supported by considerable evidence and argument, though it now appears that many observations which were attributed to the operation of a dissociative pathway may be explained equally well by other means.

In recent years, the emergence of solvent-assisted pathways has been a major advance. Even in the earliest studies[219] it was realised that solvent interactions with polar cis-$[PtX_2L_2]$ complexes would be greater than with the trans-isomers, but it was not until within the last five years that displacement of coordinated groups by solvent molecules became an accepted step in some isomerisation reactions. Displacement of tertiary phosphine by a solvent molecule, as proposed by Nelson,[232] would superficially appear to be an



unlikely process but, provided even a minute fraction of the five-coordinate species eliminate PR_3, isomerisation would eventually be achieved: that is, an equilibrium mixture of cis- and trans-$[MX_2(PR_3)_2]$ would be obtained. The question remains of how cis-$[MX_2(PR_3)_2]$ is finally produced from the trans-$[MX_2(PR_3)(S)]$ intermediate. This problem may be reduced to that of the interconversion of trans- and cis-$[MX_2(PR_3)(S)]$. This is commonly written (in general form) as a single step process

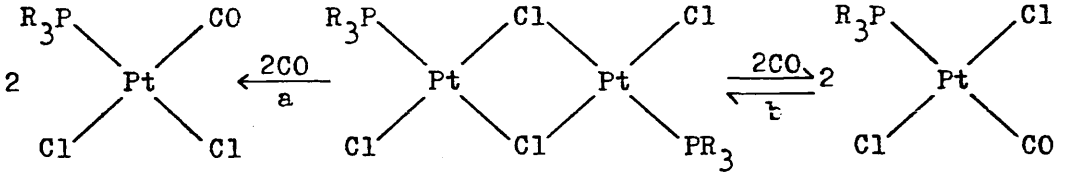


but it is probably not so simple. This is still, in fact, an isomerisation reaction of a four-coordinate complex, which may occur by either associative or dissociative means. Dissociation of the solvent molecule would produce three-coordinate species, while further solvent association would require displacement of either X^- or L, or pseudorotation of a five-coordinate species. Thus, while many isomerisation reactions probably are solvent-assisted, it is likely that the same types of mechanisms must be postulated in these cases as have been already proposed for catalysed isomerisation processes.

Results and discussion.

The complexes trans-$[PtX_2(CO)L]$ and their isomerisation.

When Chatt first reported[55] the preparation of complexes of the type cis-$[PtCl_2(CO)(PR_3)]$, obtained by passing carbon monoxide through a benzene suspension of the chloride-bridged platinum dimer, $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$, he suggested that the trans-isomer should be formed initially:[55]



(a) slow, but goes essentially to completion

(b) equilibrium favours the left-hand side

Surprisingly, the detection of such trans-complexes has not been reported to date, despite the widespread use of their cis-analogues as starting materials, probably because it was assumed that they were unstable with respect to CO loss.

Nevertheless, it was found that the complexes trans-$[PtX_2(CO)L]$ (X = Cl, L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, $AsMePh_2$ or $AsPh_3$; X = Br,

L = PMe_2Ph) could readily be generated in solution by passing carbon monoxide through suspensions of the corresponding halide-bridged dimers, $[Pt_2(\mu\text{-}X)_2X_2L_2]$, in chloroform, benzene or toluene. The reaction to form trans-$[PtX_2(CO)L]$ was generally complete in less than twenty minutes, though if passage of carbon monoxide was continued for one to two hours colourless crystals of cis-$[PtX_2(CO)L]$ were precipitated, as has been well documented.[55,198]

Since the cis-isomers are commonly prepared by the same reaction, it is not surprising that attempts to isolate the trans-complexes often resulted in cis-trans mixtures. In fact, it has not yet proved possible to obtain a pure solid sample of any of the trans-complexes, but solutions in which only trans-$[PtX_2(CO)L]$ could be detected by ir. and n.m.r. spectroscopy have been prepared. Solid samples which showed little contamination by cis-$[PtX_2(CO)L]$ or $[Pt_2(\mu\text{-}X)_2X_2L_2]$ were obtained by removal of the solvent from benzene solutions of trans-$[PtX_2(CO)L]$ at or below 0^oC, and these solids were used in certain comparative experiments.

The solution infrared spectra of the trans-$[PtX_2(CO)L]$ complexes exhibited strong $\nu(CO)$ bands in the 2130-2140 cm^{-1} region. These values are higher than those found for the corresponding cis-isomers. The ^{31}P n.m.r. parameters are similar to those of the cis-complexes, indicating that trans-halide and -carbonyl ligands have similar effects on the platinum-phosphorus bonds in the cis- and trans-$[PtX_2(CO)(PR_3)]$ complexes, respectively. The ^{13}C n.m.r. data for the complex trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ are typical for CO trans to tertiary phosphine, the large $^2J(P\text{-}C)$ value (171.7 Hz) being the most striking feature (Table 10).

When solutions of the trans-$[PtX_2(CO)L]$ complexes were allowed to stand at ambient temperature, slow conversion to the cis-isomer was detected by ir. and n.m.r. examination. Isomerisation was

^{31}P n.m.r. and ir. spectroscopic parameters

for the complexes cis- and trans-$[PtX_2(CO)L]$[a]

		cis-$[PtX_2(CO)L]$			trans-$[PtX_2(CO)L]$		
L	X	ν(CO) (cm^{-1})	δP (ppm)	^1J(Pt-P) (Hz)	ν(CO) (cm^{-1})	δP (ppm)	^1J(Pt-P) (Hz)
PEt_3	Cl	2106	22.3	2793	2135	11.6	2885
PMe_2Ph	Cl	2112	-10.4	2855	2138	-11.0	2934
PMe_2Ph	Br	2107	-11.3	2821	2132	-15.9	2825
PMe_2Ph	I	2096	-14.8	2747			
$PMePh_2$[b]	Cl	2115	-0.2	2946	2139	0.6	3000
PPh_3	Cl	2115	9.8	3061	2139	15.1	3077
$AsMePh_2$	Cl	2109			2133		
$AsPh_3$	Cl	2110			2134		

(a) n.m.r. spectra were recorded in $CDCl_3$ solution; ir. spectra were recorded in $CHCl_3$ solution

(b) the ^{13}C n.m.r. spectrum for trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ showed δC 168.3 ppm, ^1J(Pt-C) 1221 Hz and ^2J(P-C) 171.7 Hz

Table 10

generally complete after standing for between one and three days, the process apparently being faster for $[PtBr_2(CO)(PMe_2Ph)]$ and $[PtCl_2(CO)L]$ (L = PPh_3, $AsMePh_2$ or $AsPh_3$) than the others (X = Cl, L = PEt_3, PMe_2Ph or $PMePh_2$). The complex trans-$[PtI_2(CO)(PMe_2Ph)]$ could not be detected at all, in fact, passage of carbon monoxide through a chloroform suspension of the sparingly soluble iodide-bridged dimer, $[Pt_2(\mu\text{-}I)_2I_2(PMe_2Ph)_2]$, resulting in the detection of cis-$[PtI_2(CO)(PMe_2Ph)]$ only.

When a stream of nitrogen was passed through a benzene solution of trans-$[PtCl_2(CO)(PMePh_2)]$, almost total loss of carbon monoxide had occurred after five hours. This showed that free CO was present in solution, and suggested that the isomerisation process involved its generation. An identical standard solution, after the same time, contained a 1:1 mixture of cis- and trans-$[PtCl_2(CO)(PMePh_2)]$, indicating that the half-life of the trans→cis interconversion for this particular complex was of the order of five hours.

In light of the preceding discussion, it would be expected that the rate of isomerisation of the trans-$[PtX_2(CO)L]$ complexes would be affected by a number of factors. Thus, the effects of concentration, the nature of the solvent, and a variety of added ligands were studied.

Four chloroform solutions of trans-$[PtBr_2(CO)(PMe_2Ph)]$, with concentrations between 0.0125M and 0.025M, were prepared and their solution ir. spectra were recorded after 2 and 18 hours. After each time interval, all four solutions gave rise to identical spectra, suggesting that the concentration of the complex in solution is not an important factor in determining the rate of isomerisation.

An almost pure solid sample of trans-$[PtCl_2(CO)(PMePh_2)]$ was prepared, and dissolved to give 0.01M solutions in benzene and chloroform. The solution ir. spectra were recorded after $2\frac{1}{2}$, 8 and

24 hours. After 24 hours the ir.spectrum of the benzene solution exhibited only one ν(CO) band at 2104 cm^{-1}, due to cis-$[PtCl_2(CO)(PMePh_2)]$, while the chloroform solution contained a 1:1 mixture of the cis- and trans-complexes. Thus it appears that isomerisation is faster in non-polar solvents, but difficulties in observing the solution ir. spectra in other solvents have so far prevented further substantiation of this observation.

The effects of various ligands on the rate of isomerisation of trans-$[PtCl_2(CO)(PMePh_2)]$ were investigated. Continued passage of carbon monoxide through a solution of trans-$[PtCl_2(CO)(PMePh_2)]$ (prepared by passing CO through a benzene suspension of the chloride-bridged complex, $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$) resulted in almost quantitative conversion to the cis-isomer after 35 minutes, while after a similar length of time an identical standard solution was virtually unchanged. To another identical solution of trans-$[PtCl_2(CO)(PMePh_2)]$ was added 0.1 mol equiv of free $PMePh_2$ and, after 30 minutes, only cis-$[PtCl_2(CO)(PMePh_2)]$ was observed in the ir. spectrum. Partial loss of carbon monoxide was also evident, however, and this may be due to formation of some $[PtCl_2(PMePh_2)_2]$ during the reaction.

The effects of added halide ions were also studied. Introduction of 0.2 mol equiv of $Et_4N^+ Cl^-$ to a solution of trans-$[PtCl_2(CO)(PMePh_2)]$ caused 75% conversion to the cis-isomer after two hours, while about 40% reaction had occurred in a standard solution after the same time. Addition of bromide or iodide ions also increased the rate of isomerisation, 0.25 mol equiv of $Bu^n_4N^+ Br^-$ or $Bu^n_4N^+ I^-$ causing almost complete reaction within one hour. The faster isomerisation with added Br^- or I^-, as compared to that with added chloride, may at least in part be due to the greater solubility of the tetra-n-butylammonium halides.

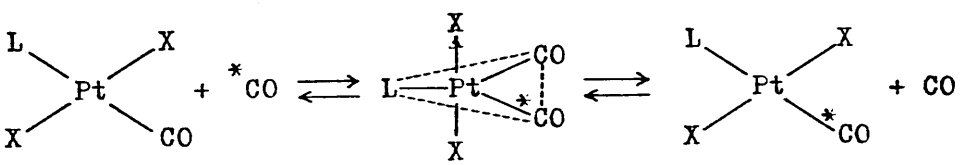
The relative rates of isomerisation and exchange of carbon monoxide were investigated by preparing a chloroform solution of trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ from labelled carbon monoxide. This exhibited a strong $\nu(^{13}CO)$ absorption at 2090 cm^{-1} ($\Delta\nu$ = -49 cm^{-1} on replacing ^{12}CO by ^{13}CO). A fraction of the solution was allowed to stand while unlabelled carbon monoxide was passed through the remainder. The solution ir. spectrum of the latter sample showed, after 15 minutes, the presence of both trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ and trans-$[PtCl_2(^{12}CO)(PMePh_2)]$, and after 25 minutes the major species in solution was trans-$[PtCl_2(^{12}CO)(PMePh_2)]$, small amounts of cis-$[PtCl_2(^{12}CO)(PMePh_2)]$ and cis- and trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ also being observed. The untreated fraction, at this stage, contained trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ only. After continuing the ^{12}CO treatment of sample 2 for a total of 35 minutes, a 1:1 mixture of cis- and trans-$[PtCl_2(^{12}CO)(PMePh_2)]$ was present, with only a weak absorption due to cis-$[PtCl_2(^{13}CO)(PMePh_2)]$ being visible. No trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ was detected in the solution after this time. The untreated solution contained a 1:1 cis-trans mixture after 13 hours, and after 38 hours only cis-$[PtCl_2(^{13}CO)(PMePh_2)]$ was detected by its strong $\nu(^{13}CO)$ band at 2065 cm^{-1} ($\Delta\nu$ = -50 cm^{-1}).

When ^{12}CO was passed through a chloroform solution of cis-$[PtCl_2(^{13}CO)(PMePh_2)]$ exchange was considerably slower, about 30% conversion to cis-$[PtCl_2(^{12}CO)(PMePh_2)]$ being achieved after one hour. Solution ir. spectra were recorded after 20 and 60 minutes, and at neither time were significant amounts of the trans-complexes observed. Thus it is apparent that exchange of CO is slow for the cis-complex, while exchange is rapid in the presence of free CO for trans-$[PtCl_2(CO)(PMePh_2)]$. Indeed, the rate of exchange is greater than the rate of isomerisation of the trans-complex.

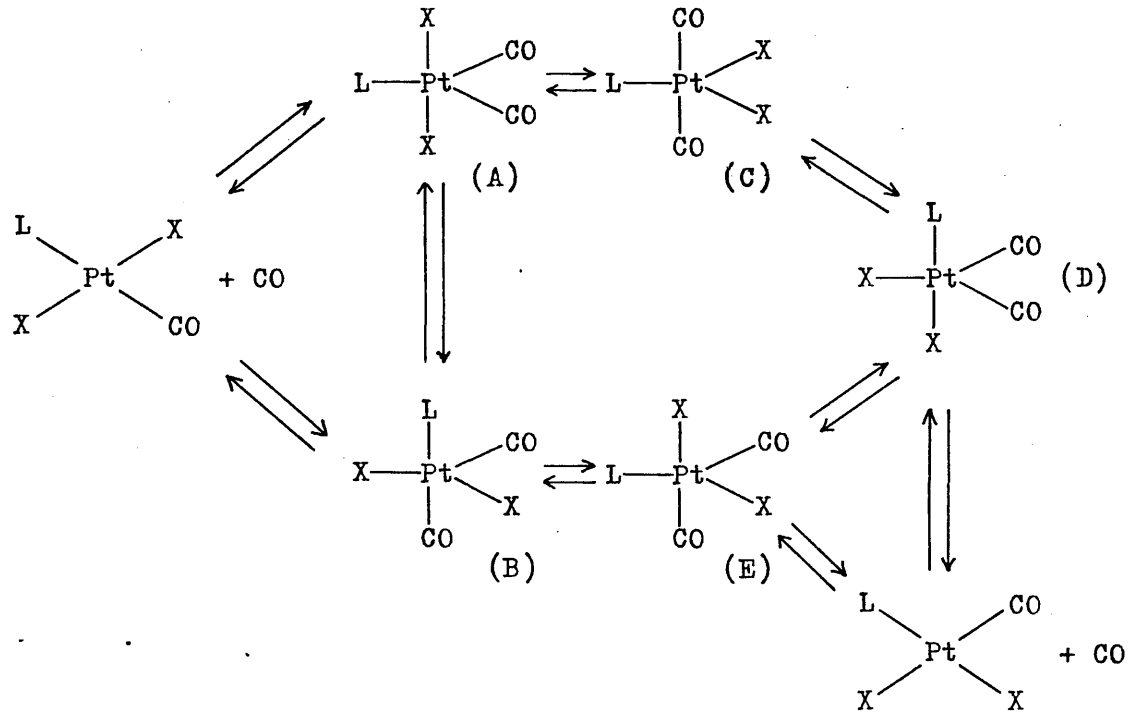
In the absence of deliberately added ligands, several points

have emerged which must be consistent with any proposed mechanism for isomerisation. The lack of any discernible concentration-dependence is indicative of an unimolecular process, that is, isomerisation does not proceed *via* interaction of two or more *trans*-$[PtX_2(CO)L]$ molecules. The production of free CO in solution, which could be swept out of solution by a stream of nitrogen, could therefore only occur *via* displacement by the solvent, or by a simple dissociation process to yield $[PtX_2L]$ which might subsequently dimerise to produce the halide-bridged complex, $[Pt_2(\mu\text{-}X)_2X_2L_2]$. Isomerisation was favoured by the non-polar solvent (that is, benzene) and, since CO elimination has already been established, it must be considered unlikely that an ionic mechanism is operative. The slower isomerisation in chloroform solution may be due to more effective solvation of the *trans*-complex or the intermediate, thereby inhibiting the reaction.

The addition of excess carbon monoxide resulted in a greatly increased rate of isomerisation, which is strongly suggestive of an associative mechanism. Thus, CO addition to form a five-coordinate species is likely to be the initial step in the process. Carbon monoxide exchange, which is faster than isomerisation, is also likely to occur in this way:

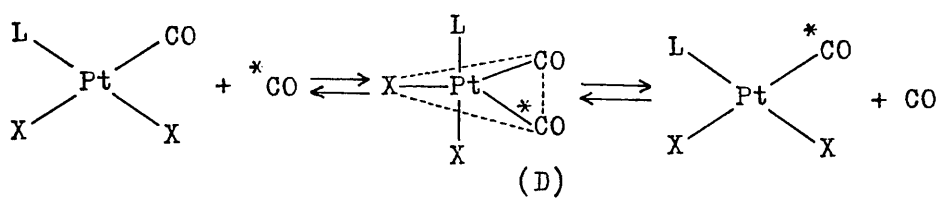


Clearly such a process will not result in isomerisation unless anion displacement or pseudorotation of the five-coordinate species takes place. Of these two, pseudorotation perhaps seems the more likely route, and might proceed in a manner similar to that outlined in Scheme 5. The five-coordinate species A is likely to be the most



Scheme 5

favoured, since it contains the tertiary phosphine or arsine and the two CO groups, which are all good π-acceptors, in the trigonal plane. It is also from intermediate A that stereospecific CO exchange might take place. Even if only a small fraction of the species A undergo pseudorotation, the remainder eliminating CO to regenerate trans-$[PtX_2(CO)L]$, total isomerisation to the cis-form would eventually be achieved. It is likely that CO exchange in cis-$[PtX_2(CO)L]$, which is much slower than for the trans-complex, would proceed via the five-coordinate intermediate D:



The presence of one π-accepting ligand, L, in an axial position

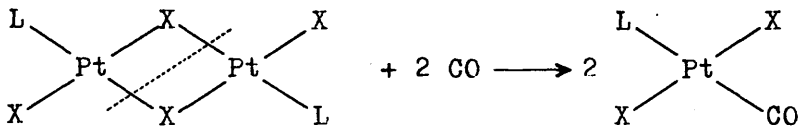
would tend to disfavour the formation of D relative to A, and this might go some way towards explaining the slower CO exchange observed for the cis-complex.

It may also be noted that the conditions of these isomerisation reactions closely resemble those proposed by Redfield and Nelson[231] as being most suited to the pseudorotation mechanism. They suggested that pseudorotation would be favoured by non-polar solvents, and where the coordinated and incoming ligand are small and of similar nucleophilicity. Indeed, the isomerisation of trans-$[PtX_2(CO)L]$ is more rapid in a non-polar solvent, and the small CO molecule is present as both coordinated and incoming ligands.

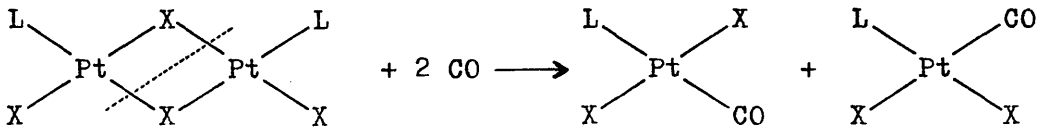
In the absence of excess carbon monoxide, it was shown that free CO was produced in solution. It seems likely, therefore, that the above mechanism should operate under these conditions also; that is, free CO attack on trans-$[PtX_2(CO)L]$ would produce a five-coordinate species which could undergo pseudorotation, ultimately giving rise to isomerisation. It might be expected that some loss of CO from the solution would occur and, indeed, this was found. Solutions monitored by ^{31}P n.m.r. spectroscopy always contained up to about 20% $[Pt_2(\mu\text{-}X)_2X_2L_2]$ at the end of the reaction.

Although the above mechanism seems to fit all the known facts, it is not the only possible means of isomerisation. A dissociative route involving CO loss, followed by rearrangement of the three-coordinate intermediate and re-combination, is also possible. A related process would be CO loss and formation of the halide-bridged dimer, $[Pt_2(\mu\text{-}X)_2X_2L_2]$. Such complexes exist as cis- and trans-isomers, and generally the equilibrium greatly favours the trans-form. They are in dynamic equilibrium, however, and if cis-$[PtX_2(CO)L]$ was formed essentially irreversibly from a small fraction of the dimer molecules, complete reaction to give the cis-complex would

eventually result. The cis- and trans-complexes are likely to be formed from the dimers as shown below:



trans



cis

Other processes, which would also involve pseudorotation of a five-coordinate species, might involve coordinated solvent or the attack of solvent on a four-coordinate molecule. Such possibilities are outlined in the following equations:

$$\underline{\text{trans}}\text{-}[PtX_2(CO)L] + S \rightleftarrows [PtX_2(CO)L(S)] \xrightarrow[\text{rotation}]{\text{pseudo-}} \underline{\text{cis}}\text{-}[PtX_2(CO)L] + S$$

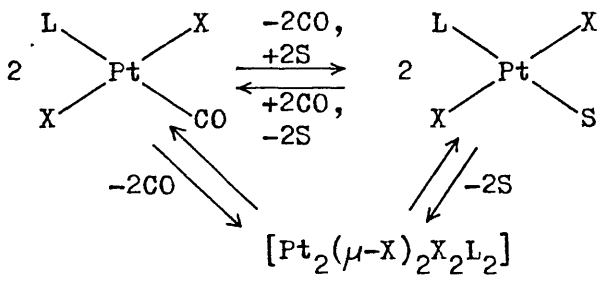
$$\underline{\text{trans}}\text{-}[PtX_2(CO)L] + S \rightleftarrows \underline{\text{trans}}\text{-}[PtX_2L(S)] + CO \longrightarrow$$

$$[PtX_2(CO)L(S)] \xrightarrow[\text{rotation}]{\text{pseudo-}} \underline{\text{cis}}\text{-}[PtX_2(CO)L] + S$$

Rearrangement of $\underline{\text{trans}}\text{-}[PtX_2L(S)]$ to its cis-form, via reversible loss of the solvent molecule, or by further solvent attack and pseudorotation of the five-coordinate species, $[PtX_2L(S)_2]$, followed by displacement of the solvent by CO, would also lead to the cis-product.

Thus, in the presence of excess carbon monoxide an associative process, involving intermediate species of the type $[PtX_2(CO)_2L]$,

is likely to be the dominant isomerisation pathway. The spontaneous isomerisation, however, may proceed by one or more of the above routes. Loss of CO, which might then attack and isomerise several trans-$[PtX_2(CO)L]$ molecules, is most likely (by analogy with the reaction in the presence of excess carbon monoxide), however, and this might be spontaneous or solvent-assisted:



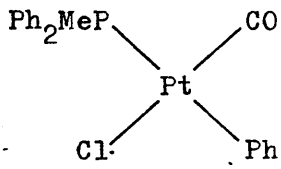
The addition of tertiary phosphine or halide ion to solutions of trans-$[PtX_2(CO)L]$ also caused rapid isomerisation. This increased rate of reaction may arise in either of two ways, both of which are associative in nature. The phosphine or halide could displace CO from the trans-complex, the free CO causing isomerisation as described previously. The ^{31}P n.m.r. spectra of such solutions indicated the presence of species of the type $[PtX_2L_2]$ or $[PtX_3L]^-$, respectively, as would be expected. Alternatively, L or X^- attack on trans-$[PtX_2(CO)L]$ to give five-coordinate species $[PtX_2(CO)L_2]$ or $[PtX_3(CO)L]^-$, respectively, which could undergo pseudorotation, would also effect isomerisation. Substitution of CO by L or X^- might occur in this case also, however, so the detection of $[PtX_2L_2]$ or $[PtX_3L]^-$ does not necessarily indicate the operation of the first process.

Thus, attack of CO on trans-$[PtX_2(CO)L]$, followed by pseudorotation of the resultant five-coordinate species, may account for the isomerisation observed in each case, but several other mechanisms are possible. Finally, it was found that the "spontaneous" reaction

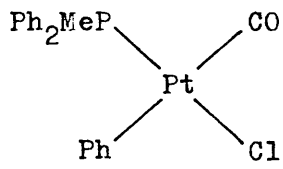
of trans-$[PtCl_2(CO)(PMePh_2)]$ to form the cis-complex was faster when exposed to sunlight than when the solution was kept dark. Also, uv. irradiation of solutions of cis- or trans-$[PtCl_2(CO)(PPh_3)]$ produced mixtures of the two isomers. It appears, therefore, that photochemically-induced isomerisation is also involved.

Isomerisation of the complexes $[PtClPh(CO)(PMePh_2)]$.

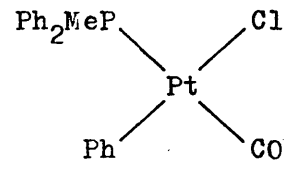
The three possible isomers of $[PtClPh(CO)(PMePh_2)]$ have been discussed in the previous chapter:



I



II



III

It was noted that isomers II and III exist in equilibrium in solution, but the mode of equilibration was not discussed in detail. A number of experiments were carried out, therefore, to attempt to gain some insight into this process.

When carbon monoxide was passed through a deuteriochloroform solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ at -60°C, the ^{31}P n.m.r. spectrum showed almost quantitative formation (ca 98%) of isomer III of $[PtClPh(CO)(PMePh_2)]$. At this temperature, no change in the spectrum with time was observed, but on warming to room temperature equilibration with isomer II took place. After one hour the ratio of II and III was about 5:1.

A sym-tetrachloroethane solution of $[PtClPh(CO)(PMePh_2)]$ (II and III) was allowed to equilibrate at room temperature, and then a stream of nitrogen was passed through the solution for four hours. After this time the solution ir. spectrum showed that about 50% loss of carbon monoxide had taken place, relative to a standard solution.

This result indicates that free CO was present in solution, and suggests the existence of a dynamic equilibrium between II and III.

Since an isomerisation reaction was involved, it seemed likely that added ligands would affect the observed rate of isomerisation from III to II. When carbon monoxide was passed through a chloroform solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ for two minutes, the solution ir. spectrum showed a strong $\nu(CO)$ absorption at 2116 cm^{-1}, due to isomer III, and a lower frequency shoulder due to isomer II. After five hours the latter band at 2106 cm^{-1} was considerably stronger, with only a shoulder at 2116 cm^{-1} being observable. When a stream of carbon monoxide through an identical solution was maintained for five hours, the band at 2116 cm^{-1} was still present as a prominent shoulder. Thus, isomerisation was slower in the presence of excess carbon monoxide.

The effects of added phosphine or halide were less obvious. When 0.2 mol equiv of PPh_3 or $Bu^n_4N^+ I^-$ was added to a solution prepared as above, the solution ir. spectrum showed some CO loss after five hours, but the rate of isomerisation was not significantly different from that in the standard solution.

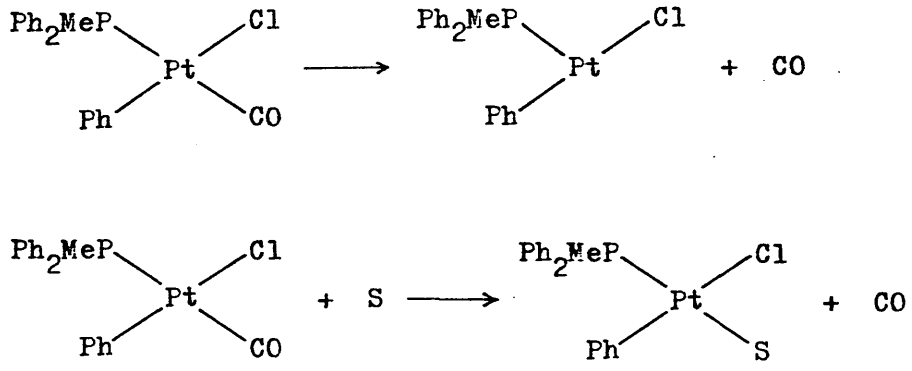
The relative rates of CO exchange and isomerisation were investigated by preparing a solution of $[PtClPh(^{13}CO)(PMePh_2)]$ in $CDCl_3$ at -60°C. The ^{31}P n.m.r. spectrum showed an initial II/III ratio of 1:5. One fraction was allowed to warm to room temperature for one hour, then cooled again to -60°C. The ^{31}P n.m.r. showed II and III to be present in the ratio 5:1. A second fraction was treated with ^{12}CO at room temperature for the same time. On cooling to -60°C, the ^{31}P n.m.r. spectrum revealed that total exchange of ^{12}CO for ^{13}CO had occurred, while isomers II and III were present in a 1:2 ratio. These results indicated that CO exchange is more rapid than isomerisation in the presence of excess carbon monoxide,

and confirmed the previous observation that the rate of isomerisation is reduced under such conditions.

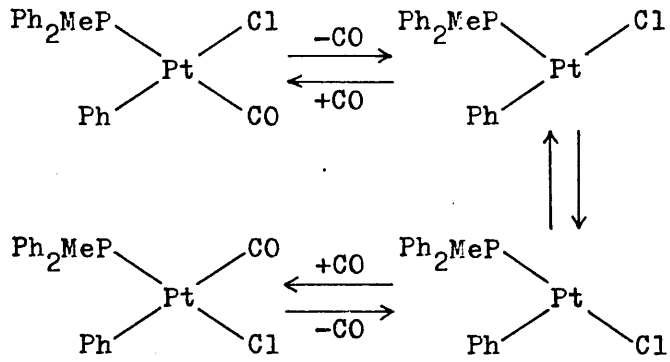
The addition of less than 0.5 mol equiv of $Et_4N^+ Cl^-$ to a third part of the solution at ambient temperature apparently had little effect on the rate of isomerisation. After one hour the ^{31}P n.m.r. spectrum showed a II/III ratio of about 9:1, but considerable loss of carbon monoxide was also evident. It is likely that displacement of CO by Cl^- to yield species of the type $[PtCl_2Ph(PMePh_2)]^-$ would account for this latter observation.

Thus, the effects of added ligands on the rate of isomerisation differ considerably from those encountered for the isomerisation of <u>trans</u>-$[PtX_2(CO)L]$ complexes. In fact, it appears that the III→II interconversion rate is significantly affected only by the addition of excess carbon monoxide (of the ligands studied), the addition of tertiary phosphine or halide ion to $[PtClPh(CO)(PMePh_2)]$ resulting in partial CO loss and no observable change in the isomerisation rate.

The reduction of isomerisation rate in the presence of excess carbon monoxide is indicative of a process involving dissociation of CO, either by direct dissociation or <u>via</u> displacement by the solvent:

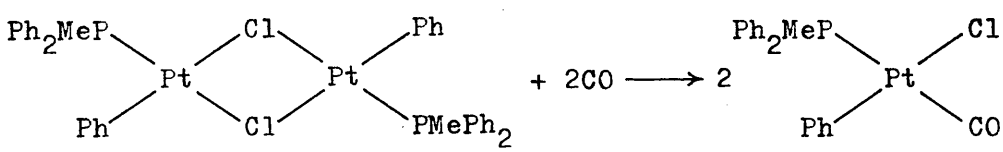


In the former case, rearrangement of the three-coordinate species followed by re-association of CO would produce isomer II:

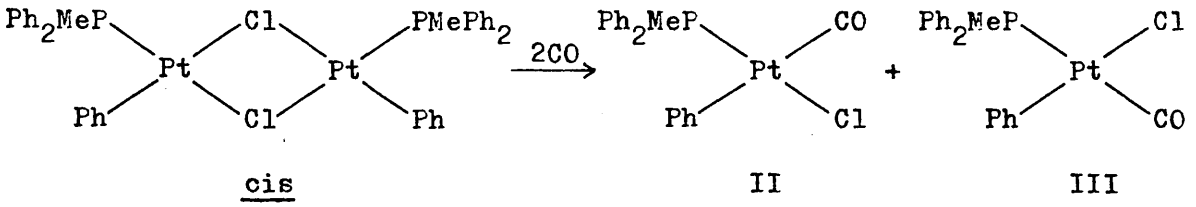


For the solvent-assisted pathway, isomerisation of $[PtClPh(PMePh_2)S]$ becomes the critical step. As noted in the previous section, this might occur by reversible loss of solvent, involving rearrangement of the $[PtClPh(PMePh_2)]$ species as above, or by association of a further solvent molecule and pseudorotation of the five-coordinate $[PtClPh(PMePh_2)(S)_2]$. Finally, solvent displacement by CO would complete the isomerisation process.

A third mechanism which might fit the observations would involve CO loss to produce the chloride-bridged complex, $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$. This is known to exist as <u>cis</u>- and <u>trans</u>-isomers, which are in dynamic equilibrium, in solution. Reaction of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ with carbon monoxide at $-60^{\circ}C$ resulted in almost quantitative formation of isomer III, but a small amount (<u>ca</u> 2%) of isomer II was also present:



<u>trans</u> III



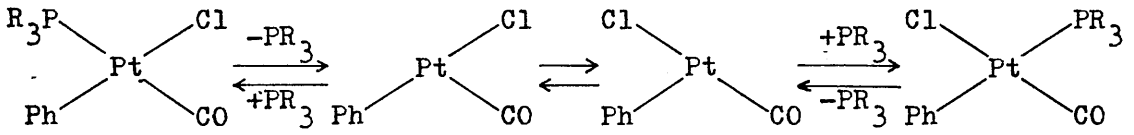
cis II III

The cis- and trans-forms of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ are found to be present in solution in the ratio 1:2 at room temperature, so it is clear that preferential reaction of the trans-form takes place. This is not exclusive, however, and if CO loss from the small amount of isomer II is slower, as seems likely from the final II/III ratio of 5.5:1 at equilibrium, eventual build-up of the amount of isomer II in solution would result.

Any one of these mechanisms would account for the faster CO exchange relative to isomerisation. After CO dissociation or displacement there would exist two competing processes; namely, isomerisation of the species thus formed, and uptake of CO by association, solvent displacement or chloride bridge cleavage. If re-incorporation of CO was faster than isomerisation, then the rapid exchange observed would follow.

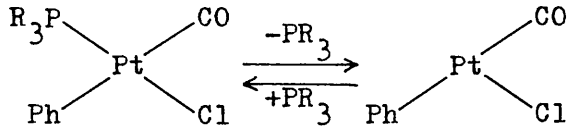
Finally, it was pointed out in the previous chapter that slow reaction of isomer II and/or III to form I, in equilibrium with the corresponding chloride-bridged aroylplatinum dimer, also occurs. This was more apparent for the complexes $[PtClPh(CO)(PPh_3)]$ (II and III), and it was suggested that reversible loss of tertiary phosphine might be involved. Such a possibility was consistent with the reaction being most rapid when the less nucleophilic PPh_3 ligand was involved. Although firm evidence for such a proposal is lacking, it seems reasonable that a route analogous to one of those outlined above should be followed. Isomerisation from either II or III to

isomer I can readily be accomodated by a solvent-assisted route incorporating pseudorotation of a $[PtClPh(CO)(S)_2]$ species. Consideration of the possible dissociative routes (direct PR_3 loss, substitution by solvent followed by solvent dissociation, or *via* dimer formation) suggests that a III→I isomerisation is more likely. Straightforward PR_3 loss from isomer III would lead to a three-coordinate species in which rearrangement *via* movement of chloride, which is likely to be the most labile ligand (and hence most prone to movement in a rearrangement process), is possible:



III I

Similarly, solvent dissociation or dimer formation and isomerisation would achieve the desired result. Loss of PR_3 from isomer II, or from the $[PtClPh(CO)(S)]$ species derived from II, would result in a species in which movement of chloride is not possible, however, and for which dimer formation is prevented:



II

Thus, unless reaction occurs *via* a $[PtClPh(CO)(S)_2]$ species, a slow isomerisation from III to I seems to be indicated. A further possibility, however, is that slow CO insertion may occur at isomer III to form $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PR_3)_2]$, and isomer I formation may simply result from equilibration with the aroylplatinum dimer.

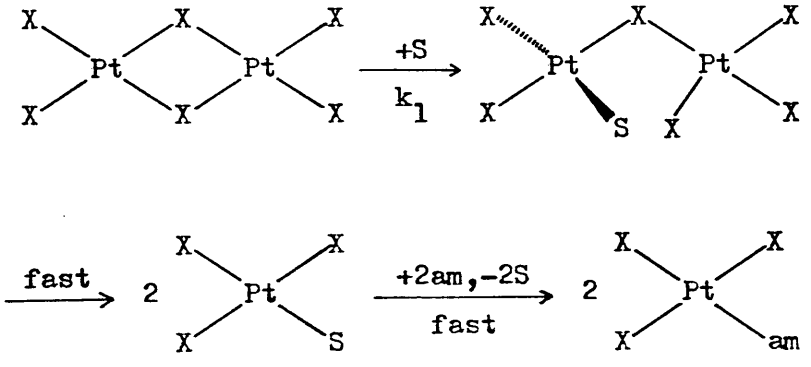
Isomerisation of halide-bridged platinum dimers.

The role of cis- and trans-forms of halide-bridged platinum dimers and their interconversion has been mentioned, in respect of their implication in the cis-trans isomerisation of monomeric platinum derivatives, in the preceding sections. Some consideration of how their interconversion might be achieved, therefore, is clearly necessary.

A kinetic study of halide-bridge cleavage by amines was carried out by Pearson and Muir in 1966. They found[249] that the rate of bridge cleavage was about 10^3 times greater than the rate of substitution in monomeric complexes, and that the rate law took the expected form for a substitution reaction:

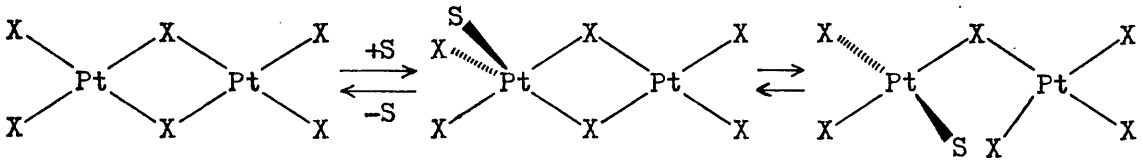
$$\text{rate} = (k_1 + k_2[\text{amine}])[\text{complex}]$$

This indicated the existence of direct and solvent-assisted substitution pathways. It was proposed that slow cleavage of one bridge by amine or solvent would be followed by a rapid second bridge cleavage. In the case of initial cleavage by solvent, the process was described as shown below:[249]

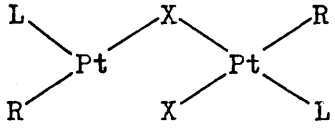


The initial step could further be described in terms of solvent attack to produce a trigonal bipyramidal species at one platinum

centre, followed by elimination of the bridging halide, both steps being reversible:[249]

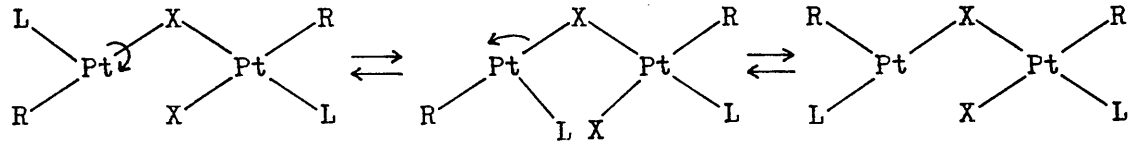


If the terminal ligands are not identical, as for example in $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ or $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$, such a reversible process might provide a mechanism for isomerisation. It seems reasonable that the solvent molecule should be only weakly held and undergo exchange, or that spontaneous single bridge opening might occur, so species of the following type would be formed in solution:



(R = Cl or Ph; L = $PMePh_2$)

The three-coordinate platinum moiety might then undergo rearrangement involving rotation about the Pt-X bond and movement of the halide to the vacant coordination site:

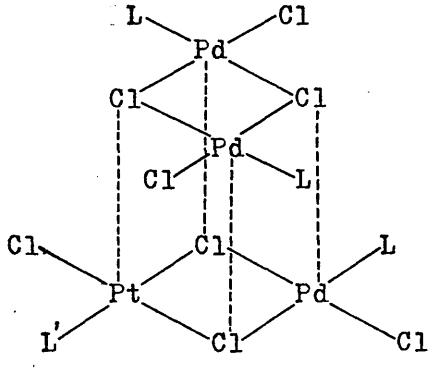


The latter re-organisation is more likely in dimeric complexes than in monomeric ones, since the bond to the bridging halide will be considerably more labile. This is reflected in the rates of halide-bridge cleavage and substitution in dimeric and monomeric complexes respectively.[249]

Although it was suggested that cleavage of the second bridge

should be fast,[249] it is likely that bridge closure would also be rapid since the entering halide ligand is already present in the same molecule. Thus during the reaction of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ with carbon monoxide, for example, single bridge opening and closure, and hence isomerisation, could be rapid compared to formation of $[PtClPh(CO)(PMePh_2)]$ (II and III). The almost quantitative production of isomer III from a mixture of cis- and trans-isomers of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ might, therefore, be explained.

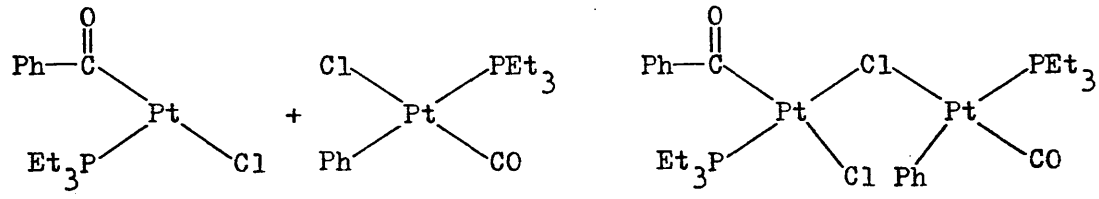
A second mechanism for halide-bridged dimer isomerisation emerged from a ^{31}P n.m.r. study of the interactions of $[Pd_2(\mu\text{-}Cl)_2Cl_2L_2]$ and $[Pt_2(\mu\text{-}Cl)_2Cl_2L'_2]$.[250] Complexes of the type $[PdPt(\mu\text{-}Cl)_2Cl_2LL']$ were observed in solution, and kinetic measurements suggested that the exchange took place via a tetrameric intermediate, formed by attack of a dimer on a dimer:



The possible involvement of singly-bridged species of the type $[LClM(\mu\text{-}Cl)MCl_2L]$ was not ruled out, however.[250] It is clear that a mechanism of this type might lead to cis-trans isomerisation of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$, for example, but the necessary cleavage and formation of four Pt-Cl bridging bonds on each occasion makes this seem a less attractive isomerisation pathway.

Finally, the single bridge-opening process can probably be related to the carbonyl insertion reactions discussed in the

previous chapter. Preliminary variable temperature ^{31}P n.m.r. studies of the complexes $[Pt_2(\mu\text{-}Cl)_2Ph_2(PEt_3)_2]$ and $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PEt_3)_2]$ have shown the rates of cis-trans isomerisation to be nearly equal for the two species, suggesting that isomerisation of the latter does not involve de-insertion of CO or the intermediacy of $[PtClPh(CO)(PEt_3)]$ (isomer I). The equilibration of $[Pt_2(\mu\text{-}Cl)_2(COPh)_2(PEt_3)_2]$ with isomer I, however, is likely to involve a singly-bridged dimer as a short-lived intermediate. It is fairly well established that reaction of $[PtClPh(CO)(PEt_3)]$ proceeds by aryl migration to give a three-coordinate species, but these species are present only in very low concentration, so it is unlikely that one such molecule would encounter another of its own kind. It is much more likely that combination of a three-coordinate species and a molecule of isomer I would occur, giving rise to a transient, singly-bridged dimeric species:



The second aryl migration step might then take place within the dimeric framework, possibly even being promoted by the incoming chloride ligand.

Experimental.

Solution infrared spectra were obtained from a Perkin Elmer 577 spectrophotometer, using 0.5mm NaCl solution cells. ^{13}C and ^{31}P n.m.r. spectra were recorded in $CDCl_3$ solution on a Varian XL-100 spectrometer, operating in the FT mode.

trans-Dichloro(carbonyl)diphenylmethylphosphineplatinum: $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ (46.6mg, 0.05 mmol) was suspended in

benzene ($5cm^3$), and carbon monoxide was passed through the suspension for 15 min. The solution ir. spectrum showed a strong absorption at 2133 cm^{-1}, and excess carbon monoxide was expelled by passing a stream of nitrogen through the solution. The solution was then frozen and the solvent removed under vacuum to leave a pale yellow solid. This was found, from its ir. spectrum, to contain a small amount of cis-$[PtCl_2(CO)(PMePh_2)]$, but was composed predominantly of the trans-complex.

The reaction was repeated several times, and an attempt was made to obtain the complex by cooling its toluene solution, but on no occasion was obtained a pure solid sample of the complex trans-$[PtCl_2(CO)(PMePh_2)]$.

Passing carbon monoxide into solutions or suspensions of $[Pt_2(\mu\text{-}X)_2X_2L_2]$ (X = Cl, L = PEt_3, PMe_2Ph, PPh_3, $AsMePh_2$ or $AsPh_3$; X = Br, L = PMe_2Ph) in chloroform for 5-20 min allowed observation, by solution ir. or ^{31}P n.m.r. spectroscopy, of the corresponding trans-$[PtX_2(CO)L]$ complexes. In each case, on standing for between 1 and 3 days, complete isomerisation to the cis-$[PtX_2(CO)L]$ complex was observed, as evidenced by the growth of an ir. absorption in the 2110 cm^{-1} region or a ^{31}P n.m.r. signal with the known δP and $^1J(Pt\text{-}P)$ values. The formation of considerable amounts of $[Pt_2(\mu\text{-}X)_2X_2L_2]$ (up to 20%) was observed for each reaction studied by ^{31}P n.m.r. spectroscopy.

Passage of nitrogen through a solution of trans-$[PtCl_2(CO)(PMePh_2)]$.

A solution of trans-$[PtCl_2(CO)(PMePh_2)]$ was prepared by passing carbon monoxide through a suspension of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ in benzene. The solution was halved, nitrogen being passed through one fraction while the other was allowed to stand. After 5 h the solution ir. spectrum showed total CO loss had occurred from the former, while the second fraction showed a 1:1 ratio of cis- and trans-complexes.

Effect of concentration on the isomerisation of trans-$[PtBr_2(CO)(PMe_2Ph)]$.

Carbon monoxide was bubbled through a solution of $[Pt_2(\mu\text{-}Br)_2Br_2(PMe_2Ph)_2]$ (49.4mg, 0.05 mmol) in chloroform (4.0cm^3) for 4 min, followed by a stream of nitrogen for 1 min. The solution ir. spectrum showed the presence of trans-$[PtBr_2(CO)(PMe_2Ph)]$ (ν(CO) 2132 cm^{-1}). A fraction of the solution was retained, the remainder being diluted to obtain samples of 0.025M, 0.020M, 0.0167M and 0.0125M concentration. Spectra were recorded after 2 and 18 h and, after each time interval, the ratio of the trans- and cis-complexes was identical in all four samples, a 1:1 ratio being obtained after 2 h.

Effect of solvent on the isomerisation of trans-$[PtCl_2(CO)(PMe_2Ph)]$.

Almost pure trans-$[PtCl_2(CO)(PMe_2Ph)]$ was prepared by passing carbon monoxide through a benzene suspension of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ and removing the solvent under vacuum at -10°C. The pale yellow solid was dissolved in benzene and chloroform to give 0.01M solutions (ν(CO) 2133 cm^{-1} and 2139 cm^{-1}, respectively), the isomerisation to the cis-complex being monitored by solution ir. spectroscopy. After 2½ h a 1:1 ratio of cis- and trans-$[PtCl_2(CO)(PMePh_2)]$ was present in benzene, while little isomerisation had occurred in chloroform solution. After 8 h the ratio of trans:cis was 1:2 in benzene and 3:1 in chloroform, while after 24 h only cis-$[PtCl_2(CO)(PMe_2Ph)]$ (ν(CO) 2104 cm^{-1}) could be observed in the benzene solution, the ratio of the two isomers being 1:1 in the chloroform solution.

Effect of added ligands on the isomerisation of trans-$[PtCl_2(CO)(PMePh_2)]$.

A solution of trans-$[PtCl_2(CO)(PMePh_2)]$ in benzene was prepared and divided into four parts. On standing for 45 min the solution ir. spectrum of the control sample showed the complex to be nearly all

in the trans-form, and after 2 h considerable cis-$[PtCl_2(CO)(PMePh_2)]$ was present (ca 40%).

1. Effect of excess carbon monoxide.

Carbon monoxide was passed through one fraction for 35 min, after which time the solution ir. spectrum showed almost total conversion to cis-$[PtCl_2(CO)(PMePh_2)]$.

2. Effect of tertiary phosphine.

Diphenylmethylphosphine (0.1 mol equiv) was added to another fraction. After 30 min only one carbonyl absorption, due to cis-$[PtCl_2(CO)(PMePh_2)]$, was observed in the ir. spectrum, although some CO loss was also evident from the decreased intensity of the absorption.

3. Effect of chloride ion.

Tetraethylammonium chloride (0.2 mol equiv) was added to the fourth fraction. The solution ir. spectra after 40 min and 2 h showed trans- and cis-$[PtCl_2(CO)(PMePh_2)]$ in the ratios 2:1 and 1:3 respectively.

In a similar experiment, to identical chloroform solutions of trans-$[PtCl_2(CO)(PMePh_2)]$ were added $Et_4N^+ Cl^-$, $Bu^n_4N^+ Br^-$ or $Bu^n_4N^+ I^-$ (0.25 mol equiv), and their solution ir. spectra were recorded after 1 h. Complete isomerisation had occurred in the last case, at least 90% and 50% reaction having taken place in the bromide and chloride systems respectively, while less than 10% conversion of trans-$[PtCl_2(CO)(PMePh_2)]$ was observed in a standard control solution. (^{31}P N.m.r. studies of similar systems showed that bromide and iodide incorporation took place, which made complete analysis of the product mixture difficult.)

Treatment of trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ with ^{12}CO.

In a $5cm^3$ flask was suspended $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMePh_2)_2]$ (18.2mg, 0.02 mmol) in chloroform ($2.0cm^3$). The system was evacuated, and

then ^{13}CO was introduced. The solution was stirred for 10 min, the solution ir. spectrum after this time showing the presence of trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ (ν(CO) 2090 cm^{-1}). The solution was divided into two parts, one fraction being allowed to stand while ^{12}CO was passed through the other.

After 15 min the latter showed the presence of trans-$[PtCl_2(^{12}CO)(PMePh_2)]$ and trans-$[PtCl_2(^{13}CO)(PMePh_2)]$, with only very weak bands due to the cis-complexes. Ten minutes later this solution contained trans-$[PtCl_2(^{12}CO)(PMePh_2)]$, some cis-$[PtCl_2(^{12}CO)(PMePh_2)]$ and little ^{13}CO-containing material. The standard solution meanwhile contained almost exclusively trans-$[PtCl_2(^{13}CO)(PMePh_2)]$. The fraction being treated with ^{12}CO showed, after 35 min, a 1:1 mixture of cis- and trans-$[PtCl_2(^{12}CO)(PMePh_2)]$, with a weak absorption due to cis-$[PtCl_2(^{13}CO)(PMePh_2)]$ (ν(CO) 2065 cm^{-1}). A 1:1 mixture of cis- and trans-$[PtCl_2(^{13}CO)(PMePh_2)]$ was obtained for the standard solution after 13 h, and only after 38 h was a single carbonyl absorption, due to cis-$[PtCl_2(^{13}CO)(PMePh_2)]$, observed ($\nu$(CO) 2065 cm^{-1}).

When a chloroform solution of cis-$[PtCl_2(^{13}CO)(PMePh_2)]$ was treated with ^{12}CO for 20 min, the solution ir. spectrum showed a weak band at 2115 cm^{-1}, due to cis-$[PtCl_2(^{12}CO)(PMePh_2)]$. The treatment was continued for a further 40 min and ca 30% conversion to cis-$[PtCl_2(^{12}CO)(PMePh_2)]$ was observed. Only very weak absorptions due to the trans-complexes were observed at any time during the reaction.

Preparation of $[PtClPh(CO)(PMePh_2)]$ (II and III) at -60°C.

A solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (27.7mg, 0.027 mmol) in $CDCl_3$ (0.5cm^3) was prepared, and cooled to -60°C. Carbon monoxide was passed through the solution for 5 min and the ^{31}P n.m.r. spectrum was recorded after 30 min and 2 h. Both spectra showed greater than

98% formation of isomer III, but a mixture in which isomer II predominated was formed after warming to room temperature for 1 h.

Treatment of $[PtClPh(CO)(PMePh_2)]$ (II and III) with nitrogen.

Passage of carbon monoxide through a sym-tetrachloroethane solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ for 5 min produced a solution of $[PtClPh(CO)(PMePh_2)]$ (II and III). The solution was halved, a strong flow of nitrogen through one fraction being maintained for 4 h. The solution ir. spectrum then showed this sample to have suffered about 50% CO loss relative to the standard solution.

Effect of added ligands on the II/III isomerisation.

A solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (30.3mg, 0.03 mmol) in chloroform ($2.0cm^3$) was prepared. Carbon monoxide was passed through the solution for 2 min, followed by a stream of nitrogen for $\frac{1}{2}$ min, and the solution was divided into four parts. One fraction was allowed to stand and its initial ir. spectrum exhibited a band at 2116 cm^{-1} with a lower frequency shoulder. After 5 h only a shoulder at 2116 cm^{-1} was visible, a much stronger absorption at 2106 cm^{-1} being present at this stage.

1. Effect of excess carbon monoxide.

Carbon monoxide was passed through one sample. After 30 min the band at 2106 cm^{-1} was very weak, the two bands being of comparable intensity after 2 h. Three hours later the 2116 cm^{-1} band was still present as a very considerable shoulder.

2. Effects of tertiary phosphine or halide ion.

Addition of PPh_3 or $Bu^n_4N^+ I^-$ (0.2 mol equiv) to the other fractions had little effect on the rate of isomerisation. The former produced solution ir. spectra identical to those of the standard solution, except that some CO loss was also apparent, while iodide addition caused some complication of the ir. spectra, presumably due to halide exchange.

Preparation of $[PtClPh(^{13}CO)(PMePh_2)]$ (II and III) at -60°C.

In a $5cm^3$ flask was prepared a solution of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (59.5mg, 0.06 mmol) in $CDCl_3$ ($1.5cm^3$). The system was evacuated and cooled to -60°C. Then ^{13}CO was admitted and the solution was stirred for 30 min. The ^{31}P n.m.r. spectrum at this temperature showed isomers II and III of $[PtClPh(^{13}CO)(PMePh_2)]$ in the ratio 1:5. The solution was then divided into three parts:

(i) One fraction was allowed to stand at ambient temperature for 1 h and then cooled again to -60°C. The ^{31}P n.m.r. spectrum then showed II and III to be present in the ratio 5:1.

(ii) Through a second fraction at 25°C was passed ^{12}CO for 1 h. On cooling to -60°C, the ^{31}P n.m.r. spectrum showed that total exchange of ^{12}CO for ^{13}CO had occurred, and isomers II and III of $[PtClPh(^{12}CO)(PMePh_2)]$ were present in the ratio 1:2.

(iii) Addition of $Et_4N^+ Cl^-$ (<0.5 mol equiv) to the third sample at room temperature gave rise, after 1 h, to a II/III ratio of ca 9:1, but a strong signal at δP 9.4 p.p.m. (^1J 2984 Hz) was also present (probably due to elimination of CO by Cl^-).

CHAPTER FIVE

Carbon-13 and Phosphorus-31 N.m.r. Spectra of Organoplatinum Complexes

Introduction.

Considerable insight into the bonding in platinum(II) complexes has been obtained by n.m.r. spectroscopy. Complexes containing phosphorus donor atoms are particularly amenable to such study, since the ^{31}P isotope is 100% abundant and has nuclear spin, $I = \frac{1}{2}$. The ^{195}Pt isotope (34% abundance) also has $I = \frac{1}{2}$, so that $^{1}J(^{195}Pt-^{31}P)$ coupling constants are also easily measured. More recently, with the advent of Fourier Transform n.m.r. spectroscopy, ^{13}C n.m.r. data have been forthcoming (^{13}C, $I = \frac{1}{2}$, 1.1% abundance) and these, too, have led to greater understanding of the bonding in platinum(II) complexes. The weight of discussion of bonding in terms of n.m.r. parameters, however, relates to the phosphorus-31 nucleus.

Understanding of ^{31}P chemical shift variations is somewhat limited, although it was suggested that, for nuclei having p- and/or d-electrons associated with them, a paramagnetic contribution to the chemical shift is dominant.[251] The other "atomic" contributions are a diamagnetic term from the atom under study, a contribution from the other atoms in the molecule, and an effect due to interatomic currents.[251,252] The chemical shifts of tertiary phosphines generally move downfield on coordination, indicating that the phosphorus atom becomes less shielded (although the opposite trend is observed for $P(OMe)_3$ and $P(OPh)_3$ complexes).

In contrast, measurements of coupling constants involving the ^{31}P nucleus have revealed considerable information about the bonding in platinum(II) complexes. The most striking use of $^{31}P-^{31}P$ coupling constants is in the assignment of *cis*- or *trans*-geometry to a complex containing magnetically non-equivalent phosphorus atoms. Such coupling constants are small in *cis*-bis(tertiary phosphine)platinum complexes, but very large in the corresponding *trans*-isomers.[253] The magnitudes of phosphorus-phosphorus coupling constants are also dependent on

the nature of the groups attached to the phosphorus atom, the nature of the metal centre, and the other ligands bonded to the metal.

It is the use of ^{195}Pt-^{31}P coupling constants as a probe, however, that has led to the most extensive discussion of bonding in platinum complexes. The coupling constant is composed of an interaction of the nuclear magnetic moments with the orbital motion of the electrons, which is generally found to be negligibly small, and a Fermi contact term. The latter refers only to σ-bonding between the atoms and, using the equation of Pople and Santry,[254] for J(Pt-P) is given by

$$J(Pt\text{-}P) \propto \gamma_{Pt}\gamma_{P}(\Delta E)^{-1}\alpha_{Pt}^{2}\alpha_{P}^{2}\left|\psi_{Pt(6s)}(0)\right|^{2}\left|\psi_{P(3s)}(0)\right|^{2}$$

where γ_{Pt} and γ_{P} are the magnetogyric ratios for the nuclei with $I = \frac{1}{2}$, ΔE is an average excitation energy, α_{X}^{2} is the s-character of the hybrid orbital used by atom X in the Pt-P bond, and $\left|\psi(0)\right|^{2}$ is the electron density of the indicated orbital at the parent nucleus. It was found that ΔE^{-1} may be regarded as being constant within a series of related compounds.[255] Large changes in α_{P}^{2} and $\left|\psi_{P(3s)}(0)\right|^{2}$ result when the groups bonded directly to phosphorus are varied, and this causes a large variation in the observed coupling constant; for example, $^{1}J(Pt\text{-}P)$ values in cis-$[PtCl_{2}(PBu_{3})_{2}]$ and cis-$[PtCl_{2}\{P(OEt)_{3}\}_{2}]$ are 3508 Hz and 5698 Hz respectively.[256] The nature of the acceptor atom, however, has little effect on α_{P}^{2} and $\left|\psi_{P(3s)}(0)\right|^{2}$ and on the coupling constant.[256]

Variations in $\left|\psi_{Pt(6s)}(0)\right|^{2}$ seem to be small, even when the system is changed extensively, and can be neglected when considering the platinum-phosphorus coupling constant. Thus, in comparing cis- and trans-$[PtCl_{2}(PBu_{3})_{2}]$ with cis- and trans-$[PtCl_{4}(PBu_{3})_{2}]$, where the 6s-orbital is shared by four and six ligands respectively, a

$(J_{Pt(IV)-P})/(J_{Pt(II)-P})$ ratio of 0.667 was predicted. Ratios of 0.59 (cis-isomers) and 0.61 (trans-isomers) were obtained,[90] and it was suggested that the closeness to the predicted value indicated that the s-character of the Pt-P bond alone determined the magnitude of the platinum-phosphorus coupling constant.[90]

Previously, the larger J(Pt-P) values in cis- rather than trans-bis(tertiary phosphine)platinum complexes had been explained in terms of π-overlap in the Pt-P bond.[257] Greater π-overlap should exist in a cis-complex since the two phosphorus atoms could use three d-orbitals (d_{xy}, d_{xz} and d_{yz}) for π-bonding, while only two d-orbitals (d_{xz} and d_{xy}) would be available in a trans-complex. Therefore, since σ- and π-bonding are synergically linked, σ-bonding ought also to be stronger in the cis-complex, giving rise to a larger coupling constant.[257]

The observation that the ratios $(J_{Pt-P}(cis))/(J_{Pt-P}(trans))$ for $[PtCl_2(PBu_3)_2]$ and $[PtCl_4(PBu_3)_2]$ were 1.47 and 1.41 respectively,[90] however, suggested that σ-bonding was similar in the two oxidation states. Since π-bonding would be expected to contribute more to the overall bonding in the lower oxidation state, it was suggested that in neither oxidation state did π-bonding make a significant contribution to the coupling constant.[90,91] Thus it was proposed that J(Pt-P) values may serve as a probe of σ-bonding only, and it was in this context that the term "trans-influence" was first coined. Furthermore, it was suggested that the magnitude of $^1J(Pt-P)$ was much more dependent on the nature of the trans-ligand than on the cis-ligand.[90]

It was subsequently proposed that there existed a correlation between $^1J(Pt-P)$ values and the corresponding Pt-P bond lengths, and it was suggested that both phenomena were affected primarily by the oxidation state of the metal, and by the nature of the trans-ligand,

both of which determine the s-character in the Pt-P bond.[181] It was later conceded, however, that appreciable changes in the coupling constants can be induced by a change of cis-ligand, though it was not clear whether some variation of $|\psi_{Pt(6s)}(0)|^2$ can occur under certain circumstances or whether cis-ligands can significantly affect the strength of the Pt-P bond.[199,258]

The existence of such a cis-influence had been proposed by Allen and Sze[259] following a ^{31}P n.m.r. study of a series of complexes of the types $[PtCl_2(PR_3)L]$ and $[PtCl(PR_3)_2L]Cl$, where L is a phosphine or phosphite ligand. It was found that the $^1J(Pt-P)$ values for the complexes cis-$[PtCl_2(PBu^n_3)L]$ were sensitive to the cis-ligand L and, considering a ligand of high cis-influence to be one which decreased the value of $^1J(Pt-P)$, a cis-influence series was compiled:[259]

$$P(OPh)_3 > P(OMe)_3 > PPh_3 > PMe_2Ph > PEt_3, PBu^n_3$$

It is generally accepted, however, that $^1J(Pt-P)$ values are a good measure of trans-influence, and that the effects of cis-ligands are of secondary importance. The relationship between $^1J(Pt-P)$ values and trans-influence has been discussed in a number of reviews.[89,92,93]

Results and discussion.

N.m.r. spectra of platinum carbonyl complexes.

Carbon-13 n.m.r. spectra have been reported for a number of carbonyl complexes of platinum, and ^{31}P n.m.r. data have been tabulated where tertiary phosphine was present as a supporting ligand. Such studies have included a considerable number of cationic complexes, trans-$[PtX(CO)L_2]^+$ (L = tertiary phosphine or arsine; X = halide, alkyl or aryl),[200,260-264] a few neutral complexes of

the types cis-$[PtX_2(CO)L]$ and $[PtX_2(CO)_2]$,[200,262] and some anionic species of the types $[PtX_3(CO)]^-$ and cis-$[PtCl_2R(CO)]^-$ (R = alkyl or aryl).[262,265] It was found that δC decreased with increasing negative charge on the complex, and that in trans-$[PtX(CO)L_2]^+$ complexes $^1J(Pt-C)$ was strongly influenced by the nature of the trans-ligand X.[200] The effects of cis- and trans-ligands and the charge on the complex on the n.m.r. parameters, however, had not been thoroughly investigated.

A systematic study of the effects of cis- and trans-ligands on the ^{13}C and ^{31}P n.m.r. parameters of neutral platinum carbonyl complexes was therefore carried out using the complexes discussed in previous chapters, and comparisons made with the cationic and anionic complexes previously reported.

The ^{13}C and ^{31}P n.m.r. data for the cis- and trans-$[PtX_2(CO)L]$ complexes are given in Tables 11 and 12, while those for the three isomers of $[PtXR(CO)L]$ are given in Tables 13 to 15. Comparison of the ^{31}P chemical shifts of a set of corresponding complexes in Tables 11 to 15 reveals no systematic variations. The ^{13}C chemical shifts, however, appear to be sensitive to changes in either cis- or trans-ligands. A comparison of complexes 1, 14, 19, 34 and 40, for example, shows that δC increases from 157.4 p.p.m. when CO is trans to Cl (1), to 169.9 p.p.m. trans to PEt_3 (14) and 178.1 p.p.m. trans to Ph (34). Similar variations have been reported for cationic complexes.[200]

It may also be noted that δC increases from 157.4 p.p.m. when CO lies cis to Cl (1) to 163.1 p.p.m. cis to Ph (19) (both with CO trans to Cl and cis to PEt_3), and from 169.9 p.p.m. cis to Cl (14) to 174.4 p.p.m. cis to Ph (40) (both with CO trans to PEt_3 and cis to Cl). A comparison of the $[PtCl_3(CO)]^-$ anion[262] with the complexes cis-$[PtCl_2(CO)(PMe_3)]$ and trans-$[PtCl(CO)(PMe_3)_2]^+$ [200] shows a trend

^{13}C and ^{31}P n.m.r. data for the complexes cis-$[PtX_2(CO)L]$

	X	L	δC (ppm)	^1J(Pt-C) (Hz)	^2J(P-C) (Hz)	δP (ppm)	^1J(Pt-P) (Hz)
1	Cl	PEt_3	157.4	1751	6.7	22.3	2793
2	Br	PEt_3	157.8	1734	4.9		
3	I	PEt_3	158.8	1664	3.6		
4	Cl	PMe_2Ph	156.8	1773	6.8	-10.4	2855
5	Br	PMe_2Ph				-11.2	2822
6	I	PMe_2Ph				-14.7	2748
7	Cl	$PMePh_2$	156.3	1764	6.4	-0.2	2946
8	Cl	PPh_3	156.5	1755	6.4	9.8	3061
9	Cl	PCy_3				36.4	2850
10	Cl	$P(o\text{-tolyl})_3$				5.6	3010
11	Cl	$AsMePh_2$	155.3	1730			
12	Cl	$AsPh_3$	155.4	1719			
13	Cl	pyridine	155.4	1879			

Table 11

^{13}C and ^{31}P n.m.r. data for the complexes <u>trans</u>-$[PtX_2(CO)L]$

	X	L	δC (ppm)	^1J(Pt-C) (Hz)	^2J(P-C) (Hz)	δP (ppm)	^1J(Pt-P) (Hz)
14	Cl	PEt_3	169.9	1164	159.6	11.6	2885
15	Cl	PMe_2Ph				-11.0	2933
16	Br	PMe_2Ph				-15.9	2825
17	Cl	$PMePh_2$	168.3	1221	171.7	0.6	3000
18	Cl	PPh_3				15.1	3077

Table 12

^{13}C and ^{31}P n.m.r. data for the complexes [PtXR(CO)L] (isomer I)

	X	R	L	δC (ppm)	^{1}J(Pt-C) (Hz)	^{2}J(P-C) (Hz)	δP (ppm)	^{1}J(Pt-P) (Hz)
19	Cl	Ph	PEt_3	163.1		8.5	18.9	1407
20	Br	Ph	PEt_3	162.7		8.8		
21	I	Ph	PEt_3	162.4				
22	Cl	Ph	PMe_2Ph	162.4		7.9	-5.3	1381
23	Cl	CH_2Ph	PMe_2Ph				-3.3	1402
24	Cl	Ph	$PMePh_2$ [a]	162.1	1947	8.2	6.8	1402
25	Br	Ph	$PMePh_2$				2.9	1436
26	Cl	Me	$PMePh_2$	164.8	1950	7.4	12.1	1449
27	Cl	Et	$PMePh_2$	165.7		7.3	12.1	1449
28	Cl	CH_2Ph	$PMePh_2$	163.9		9.0	8.4	1414
29	Cl	Ph	PPh_3	162.3	1947	7.4	18.9	1426
30	Cl	Ph	PCy_3				31.0	1437
31	Cl	Ph	$P(\underline{o}\text{-tol})_3$				17.9	1366
32	Cl	Ph	$AsMePh_2$	161.5	1945			
33	Cl	Ph	$AsPh_3$	161.6	1943			

(a) $\delta^{195}Pt$ -515.5 ppm, obtained from the $^{1}H-\{^{31}P\}$ n.m.r. spectrum.

Table 13

^{13}C and ^{31}P n.m.r. data for the complexes [PtXPh(CO)L] (isomer II)

	X	L	δC (ppm)	^1J(Pt-C)/Hz 25°C	-60°C	^2J(P-C) (Hz)	δP (ppm)	^1J(Pt-P) (Hz)
34	Cl	PEt_3	178.1	909	923	6.1	12.5	3700[a]
35	Cl	PMe_2Ph	177.6	906	924	5.9		
36	Br	PMe_2Ph					-14.4	3770
37	Cl	$PMePh_2$[b]	177.4	906		6.1	-1.7	3920
38	I	$PMePh_2$					-1.6	3699
39	Cl	PPh_3	177.7	895±5	909	6.3	10.2	4071

(a) at -60°C, ^1J(Pt-P) 3691 Hz

(b) δPt -737.2 ppm, obtained from the ^1H-{^{31}P} n.m.r. spectrum

Table 14

^{13}C and ^{31}P n.m.r. data for the complexes [PtXPh(CO)L] (isomer III)

	X	L	δC (ppm)	^{1}J(Pt-C)/Hz 25°C	^{1}J(Pt-C)/Hz -60°C	^{2}J(P-C) (Hz)	δP (ppm)	^{1}J(Pt-P) (Hz)
40	Cl	PEt_3	174.4	1352	1345	148.4	12.1	3337[a]
41	Cl	PMe_2Ph	173.8	1390	1384	157.5		
42	Br	PMe_2Ph					-10.1	3359
43	Cl	$PMePh_2$[b]	173.3	1427		157.8	5.7	3481
44	Cl	PPh_3	172.4[c]		1461	155.6[c]	20.1	3561

(a) at -60°C; ^{1}J(Pt-P) 3297 Hz

(b) δPt -649.7 ppm, obtained from the $^{1}H-\{^{31}P\}$ n.m.r. spectrum

(c) at -60°C

Table 15

of similar magnitude. This involves replacement of a cis-chloride by tertiary phosphine and a simultaneous increase in positive charge, and therefore suggests that the nature of the cis-ligand is more important than the overall charge on the complex in determining the ^{13}C chemical shift.

The value of $^{1}J(Pt-P)$ is very sensitive to the other ligands and the geometry of the complex. The trans-ligand exerts a considerable influence on the coupling constant, as was pointed out previously for [PtXR(CO)L] (isomer I), where the low $^{1}J(Pt-P)$ value was attributed to the high trans-influence of R. Thus, $^{1}J(Pt-P)$ decreases from 3700 Hz when PEt_3 lies trans to Cl in complex 34, to 3337 Hz trans to CO (40), and finally to 1407 Hz trans to Ph (19). The dramatic reduction in the last case is doubtless due mainly to the high trans-influence of the phenyl group. The $^{1}J(Pt-P)$ coupling constant is also sufficiently sensitive to reflect the trans-influence variations within the halide series. Thus, the value of 2855 Hz in cis-$[PtCl_2(CO)(PMe_2Ph)]$ (complex 4) decreases to 2822 Hz and 2748 Hz when the trans- (and cis-) chloride is replaced by bromide (5) and iodide (6) respectively.

It is apparent, however, that the value of $^{1}J(Pt-P)$ is significantly affected by the nature of the cis-ligands, and this has previously been discussed with reference to the complexes cis-$[PtCl_2(PEt_3)L]$.[177] It is found that $^{1}J(Pt-P)$ values decrease from 3515 Hz in cis-$[PtCl_2(PEt_3)_2]$ to 2793 Hz in cis-$[PtCl_2(CO)(PEt_3)]$, and it was suggested that this cis-influence of CO reflects its π-acidity, in that competition between CO and PEt_3 for the metal d-electrons takes place.[177] Thus the nearly equal $^{1}J(Pt-P)$ values found for cis- and trans-$[PtX_2(CO)L]$ complexes may result primarily from the π-bonding ability of CO in the cis-position in the former.

Change of a cis-ligand from halide to an organic group causes

an increase in $^{1}J(Pt-P)$, which is the reverse of the observed effect of a similar ligand change in the trans-position. Thus $^{1}J(Pt-P)$ increases from 2885 Hz in trans-$[PtCl_2(CO)(PEt_3)]$ (14) to 3337 Hz in $[PtClPh(CO)(PEt_3)]$ (isomer III; 40), and from 2793 Hz in cis-$[PtCl_2(CO)(PEt_3)]$ (1) to 3700 Hz in $[PtClPh(CO)(PEt_3)]$ (isomer II; 34). The larger increase in the latter case may be due to weakening of the Pt-CO interaction by the trans phenyl group, thereby reducing the cis-influence of CO on the Pt-P bond. Similar effects of a cis organic group have been observed in bis(tertiary phosphine)platinum complexes where $^{1}J(Pt-P)$ increases from 2435 Hz in trans-$[PtCl_2(PEt_3)_2]$[266] to 2816 Hz in trans-$[PtClMe(PEt_3)_2]$,[267] and from 3548 Hz in cis-$[PtCl_2(PMe_2Ph)_2]$ to 4250 Hz in cis-$[PtClMe(PMe_2Ph)_2]$ (trans to Cl).[267]

The values of $^{1}J(Pt-C)$ are also dependent on both the cis- and trans-ligands. These are found to decrease from ca 1950 Hz when CO lies trans to halide to ca 900 Hz trans to phenyl. For example, $^{1}J(Pt-C)$ decreases from 1947 Hz in complex 24 (CO trans to Cl), to 1427 Hz trans to $PMePh_2$ (43) and to 906 Hz trans to Ph (37). The $^{195}Pt-^{13}C$ coupling constant is also sensitive enough to show a steady decrease as the trans- (and cis-) halide is changed from chloride to bromide or iodide (complexes 1, 2 and 3). Similar trends for changes in the trans-ligands have been observed for the cationic complexes[200,260-264] trans-$[PtX(CO)L_2]^{+}$, and the anionic complexes[262] $[PtX_3(CO)]^{-}$.

On changing the ligand cis to CO from halide to an organic group, a significant increase in $^{1}J(Pt-C)$ is observed (as was found for $^{1}J(Pt-P)$ when the cis-ligand was varied). Thus, for example, replacing one chloride ligand in cis-$[PtCl_2(CO)(PMePh_2)]$ by phenyl (24) results in an increase from 1764 Hz to 1947 Hz; similarly, $^{1}J(Pt-C)$ in trans-$[PtCl_2(CO)(PMePh_2)]$ is 1221 Hz, but replacement

of one chloride by phenyl to produce $[PtClPh(CO)(PMePh_2)]$ (isomer III; 43) causes this to increase to 1427 Hz. For anionic carbonyl complexes, $^1J(Pt-C)$ increases from 1732 Hz[262] in $[PtCl_3(CO)]^-$ to 2042 Hz[265] in cis-$[PtCl_2Ph(CO)]^-$.

It is apparent, therefore, that cis-ligands exert a marked influence on $^1J(Pt-C)$ and $^1J(Pt-P)$, though the mechanism by which it is exerted is not well understood. It is not simply related to the σ-bond strength, as is apparently that of the trans-influence.[89,92] What is clear, however, is that the magnitude of the effect produced by cis-ligand variations is such that extreme caution must be exercised when attempting to relate one-bond coupling constants to the trans-influence of the trans-ligand.

Tables 14 and 15 reveal that the coupling constants $^1J(Pt-C)$ and $^1J(Pt-P)$ of the complexes $[PtClPh(CO)L]$ (II and III) are temperature-dependent. Temperature variations in $^1J(Pt-P)$ have been reported for the complexes cis- and trans-$[PtCl_2(PBu^n_3)_2]$, and it was suggested[268] that they originated in a change of hybridisation at platinum brought about by solvation. Increasing temperature would reduce solvation and lead to an increased coupling constant, as was observed.[268] The complexes $[PtClPh(CO)(PEt_3)]$ (II and III) show similar variations in their $^1J(Pt-P)$ coupling constants. Thus complex 34 has a $^1J(Pt-P)$ value of 3700 Hz at 25°C, which decreases to 3695 Hz at -20°C, and 3691 Hz at -60°C; similarly the $^1J(Pt-P)$ value for complex 40 decreases from 3337 Hz at 25°C, to 3314 Hz at -20°C, and 3297 Hz at -60°C. A similar temperature effect on $^1J(Pt-C)$ is found for the complexes in Table 15, but $^1J(Pt-C)$ values for the complexes $[PtClPh(CO)L]$ (isomer II; Table 14) experience an inverse temperature-dependence, increasing by ca 15 Hz when the temperature is reduced from +25°C to -60°C. This inverse relationship is not consistent with a simple explanation in terms of extent of solvation,

and thus it seems that the reason for the temperature dependence of coupling constants must be more complex than was previously thought.

The values of $^{2}J(P-C)$ are extremely sensitive to the stereochemistry of the complexes. The compounds in Tables 12 and 15, with CO trans to tertiary phosphine, exhibit $^{2}J(P-C)$ values in excess of 140 Hz, while the other complexes, with a cis-arrangement of CO and tertiary phosphine ligands, typically show values of less than 10 Hz. Such enhanced coupling to trans-phosphine groups is well-known at platinum and has been observed, for example, in phosphorus-phosphorus coupling[259,269] and phosphorus-hydrogen coupling,[214] though such examples involving phosphorus-carbon coupling are less common.[260] These are, in fact, the first examples of coupling between mutually trans tertiary phosphine and carbonyl ligands. No clear pattern emerges, however, from the magnitudes of $^{2}J(P-C)$ for complexes in which CO and tertiary phosphine occupy mutually cis-positions. This is not surprising since the trans-influences of both the other ligands will exert an effect on the two bonds concerned.

The relative signs of the $^{1}J(Pt-P)$, $^{1}J(Pt-C)$ and $^{2}J(P-C)$ coupling constants, along with the ^{195}Pt chemical shifts, were determined for complexes 1, 14, 34 and 40, which had been prepared using labelled ^{13}CO, by double resonance methods.[270] For the $^{13}C-^{31}P-^{195}Pt$ three-spin system, observation of the ^{31}P n.m.r. spectrum while irradiating the ^{195}Pt nucleus allowed the magnitudes and relative signs of $^{2}J(P-C)$ and $^{1}J(Pt-C)$ to be obtained. Similarly, irradiation of the ^{13}C nucleus permitted those of $^{1}J(Pt-P)$ and $^{1}J(Pt-C)$ to be determined.[271] The ^{195}Pt chemical shifts were also obtained by $^{31}P-\{^{195}Pt\}$ double resonance methods. The results of these studies are given in Table 16. The absolute signs of $^{1}J(Pt-C)$ and $^{2}J(P-C)$ were obtained by comparison with the signs of the $^{1}J(Pt-P)$ coupling constants, which are known to be positive.[267,272-276]

Thus in all four complexes the $^{1}J(Pt-C)$ coupling constants were found to be positive. Previous attempts to determine the signs of $^{1}J(Pt-C)$ coupling constants have been few to date. It was found, however, that $^{1}J(Pt-C)$ in $[PtCl_3(C_2H_4)]^-$ had a value of +192 Hz,[277] and it was argued on the basis of a theoretical calculation that the value of 1757 Hz obtained for $[PtCl_3(CO)]^-$ should also be positive.[277] Previously it had been inferred that the two types of π-bonded carbons (cis or trans to Me) in the complexes [PtXMe(cod)] gave rise to $^{1}J(Pt-C)$ values of opposite signs,[278] and it was suggested that the sign of $^{1}J(Pt-C)$ in olefinplatinum complexes depends on the nature of the olefin and of the trans-ligand.[277,278] The examples given in Table 16, however, are the first platinum carbonyl complexes for which the sign of $^{1}J(Pt-C)$ has been unambiguously determined, and it appears that it is not affected by the nature of the ligand trans to the carbonyl group.

It has been found for the complex cis-$[PtMe_2(PMe_2Ph)_2]$ that a methylplatinum ^{13}C nucleus is strongly coupled to one phosphorus atom but weakly coupled to the other, and that the two $^{2}J(P-C)$ coupling constants were of opposite sign.[279] It was assumed that the larger value was due to coupling to the trans ^{31}P nucleus, and indeed it was later noted that large $^{2}J(P-C)$ values were obtained for mutually trans carbon and phosphorus ligands in platinum complexes,[280] but the absolute signs of the two coupling constants were not determined.[279]

The complexes in Table 16 are thus the first platinum species for which the absolute signs of $^{2}J(P-C)$ coupling constants have been obtained. The large values observed when CO lies trans to PEt_3 (complexes 14 and 40) are of positive sign, while small, negative values of $^{2}J(P-C)$ are found when CO and PEt_3 occupy mutually cis-positions (1 and 34). Thus, both the magnitudes and the signs of

^{13}C, ^{31}P and ^{195}Pt n.m.r. data - signs of coupling constants

	complex	δP/ppm	^{1}J(Pt-P)/Hz	^{2}J(P-C)/Hz	δC/ppm	^{1}J(Pt-C)/Hz	δPt/ppm[a]
1	cis-$[PtCl_2(^{13}CO)(PEt_3)]$	22.3	+2793	-6.7	157.4	+1749	-656.1
14	trans-$[PtCl_2(^{13}CO)(PEt_3)]$	11.6	+2883	+159.6	169.9	+1164	-289.0
34	$[PtClPh(^{13}CO)(PEt_3)]$ (II)	12.4	+3702	-6.0		+909	-794.3
40	$[PtClPh(^{13}CO)(PEt_3)]$ (III)	12.1	+3336	+148.4		+1352	-616.8

(a) reference: $\Xi(Pt)$ = 21,420,980 Hz for cis-$[PtCl_2(SMe_2)_2]$ (ref. 266)

Table 16

^{2}J(P-C) coupling constants depend on the stereochemistry of the complex and, in particular, on the relative positions of the CO and PEt_3 ligands. It is likely that the signs of ^{2}J(P-C) coupling constants should show similar trends to those of ^{2}J(P-P) coupling constants, and the latter have been discussed in some detail.[253,281]

The ^{195}Pt chemical shifts of cis- and trans-$[PtCl_2(CO)(PEt_3)]$ differ by 367 p.p.m. (Table 16), so this parameter would also be suitable for differentiating between the two isomers. Similarly, a significant difference exists between the ^{195}Pt chemical shifts of isomers II and III of $[PtClPh(CO)(PEt_3)]$. The corresponding shifts for isomers II and III of $[PtClPh(CO)(PMePh_2)]$ (complexes 37 and 43) are similar, while that for isomer I of $[PtClPh(CO)(PMePh_2)]$ (complex 24) differs by over 100 p.p.m. Thus, identification of the three isomers of [PtXR(CO)L] might also be possible using their ^{195}Pt chemical shifts. Interpretation of ^{195}Pt chemical shift data, however, has met with limited success to date.[266,267,282]

N.m.r. spectra of the complexes trans-$[PtX(COR)L_2]$.

The ^{13}C and ^{31}P n.m.r. data are given in Table 17. The values of ^{1}J(Pt-P) are considerably higher than those for the complexes trans-$[PtX_2(PR_3)_2]$,[266] indicating once again the importance of the nature of the cis-ligand. Where complexes were prepared, for which comparisons could be made, the coupling constants are higher than those in the corresponding alkyl- or arylplatinum complexes. Thus, while trans-$[PtClPh(PMePh_2)_2]$ has a ^{1}J(Pt-P) value of 3010 Hz (δP 8.7 p.p.m.), the corresponding benzoylplatinum species has a value of 3215 Hz; similarly trans-$[PtClEt(PMePh_2)_2]$ exhibits a coupling constant of 3235 Hz (δP 14.2 p.p.m.), and a value of 3344 Hz is observed for the propionylplatinum derivative. Therefore it appears that cis-acyl or -aroyl ligands exert a greater influence on the platinum-phosphorus bond, as evidenced by a change in ^{1}J(Pt-P),

^{13}C and ^{31}P n.m.r. data for the complexes trans-$[PtX(COR)L_2]$

X	R	L	δC (ppm)	^1J(Pt-C) (Hz)	^2J(P-C) (Hz)	δP (ppm)	^1J(Pt-P) (Hz)
Cl	Ph	PEt_3	213.6	1064	6.1		
Br	Ph	PEt_3	214.0	1068	5.7		
I	Ph	PEt_3	216.6	1054	ca 5		
Cl	Ph	PMe_2Ph	213.8	1028	6.4		
Cl	Et	PMe_2Ph				-6.4	3174
Cl	Ph	$PMePh_2$	212.9	1007	6.1	5.1	3215
Cl	Me	$PMePh_2$	216.9	928[a]	ca 5		
Cl	Et	$PMePh_2$	218.0	928[b]	ca 5	6.2	3344
Cl	CH_2Ph	$PMePh_2$				5.6	3307
Cl	Ph	PPh_3	212.6	993	5.7		

(a) at -40°C, ^1J(Pt-C) 934 Hz

(b) at -40°C, ^1J(Pt-C) 937 Hz

Table 17

than do cis-alkyl or -aryl groups.

The value of $^{1}J(Pt-C)$ would be expected to reflect the s-character of the platinum-carbon bond and, therefore, should decrease as the carbon atom hybridisation changes from sp to sp^2 to sp^3. While keeping the trans-ligand constant, many examples may be cited which would suggest that this is indeed found to be so. Values of $^{1}J(Pt-C)$ of 1764 Hz in cis-$[PtCl_2(CO)(PMePh_2)]$ (Table 11), 1788 Hz[200] in trans-$[PtCl(CO)(PPh_3)_2]^+$, 1726 Hz in cis-$[PtCl_2(CNMe)(PEt_3)]$ and 1720 Hz[263] in trans-$[PtCl(CNMe)(PEt_3)_2]^+$ have been found, the carbon atom being formally sp-hybridised in each case.

For sp^2-hybridised carbon, $^{1}J(Pt-C)$ values of 1007 Hz in trans-$[PtCl(COPh)(PMePh_2)_2]$ (Table 17), 1125 Hz in trans-$[PtCl\{C(OMe)Me\}(AsMe_3)_2]^+$ and 1047 Hz[283] in trans-$[PtCl\{C(NHMe)Me\}(AsMe_3)_2]^+$ were obtained, while a value of 673 Hz was found for the sp^3-hybridised carbon atom in trans-$[PtClMe(PMe_2Ph)_2]$.[260] For the complexes trans-$[PtClPh(AsMe_3)_2]$ and trans-$[PtCl(CO_2Me)(PPh_3)_2]$, however, where the carbon atom is formally sp^2-hybridised, the $^{1}J(Pt-C)$ coupling constants are 858 Hz[261] and 1346 Hz[200] respectively, suggesting that a wide range of $^{1}J(Pt-C)$ values is spanned by sp^2-hybridised carbon atoms. A change of trans-ligand, as for the complexes trans-$[PtCl\{C(OMe)Me\}(AsMe_3)_2]^+$ and trans-$[PtMe\{C(OMe)Me\}(AsMe_3)_2]^+$ ($^{1}J(Pt-C)$ coupling constants 1125 Hz and 759 Hz[283] respectively), can have an effect on $^{1}J(Pt-C)$ of similar magnitude to that produced by a change in hybridisation of the carbon atom and, as pointed out previously, a change of cis-ligand can cause an effect of almost comparable magnitude.

The chemical shift values, δC, apparently show little dependence on carbon atom hybridisation. The acylplatinum complexes have chemical shifts around 215 p.p.m. (Table 17); that is, to lower field than the carbonyl derivatives described above (155 to 178 p.p.m.),

and to lower field than some other sp^2-hybridised carbon ligands such as phenyl (120 to 140 p.p.m.)[261] and alkoxocarbonyl (ca 170 p.p.m.).[200] Ligand carbene carbon atoms are generally found to even lower field (200 to 300 p.p.m.),[283] however, while for the sp^3-hybridised carbon atom in methylplatinum complexes the ^{13}C resonance is found to much higher field (-30 to 0 p.p.m.).[260] Thus, sp^2-hybridised carbon resonances span a large range of chemical shift values, and it appears that no simple relation exists between chemical shift and carbon atom hybridisation for organoplatinum complexes.

N.m.r. spectra of the complexes $[Pt_2(\mu\text{-}X)_2R_2L_2]$.

Complexes of the type $[Pt_2(\mu\text{-}X)_2(COR)_2L_2]$ (X = Cl, Br, I or SCH_2Ph; R = Me, Et or Ph; L = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3 or PCy_3) were prepared as described previously, and exist in solution with isomer I of [PtXR(CO)L]. The complexes $[Pt_2(\mu\text{-}X)_2Ph_2L_2]$ (X = Cl, L = PEt_3, $PMePh_2$ or PPh_3; X = Br, L = PMe_2Ph; X = I, L = $PMePh_2$) were prepared by treating $[Pt_2(\mu\text{-}X)_2X_2L_2]$ with $HgPh_2$. Their n.m.r. data are given in Tables 18 and 19 respectively, and these reveal several points of interest.

Perhaps the most striking parameters are the very large $^1J(Pt\text{-}P)$ values observed in the ^{31}P n.m.r. spectra of all the complexes. Indeed several unusually large $^1J(Pt\text{-}P)$ values in halide-bridged platinum complexes have recently been reported.[193,202] For the complexes $[Pt_2(\mu\text{-}X)_2(COPh)_2(PMePh_2)_2]$ (X = Cl, Br, I or SCH_2Ph), the values of $^1J(Pt\text{-}P)$ decrease in the following order:

$$Cl > Br > I > SCH_2Ph$$

This is the reverse of the trans-influence series for these ligands (at least in mononuclear platinum(II) complexes), and it is quite

^{13}C and ^{31}P n.m.r. data for the complexes $[Pt_2(\mu\text{-}X)_2(COR)_2L_2]$[a]

X	R	L	δC (ppm)	^1J(Pt-C) (Hz)	^2J(P-C) (Hz)	δP (ppm)	^1J(Pt-P) (Hz)
Cl	Ph	PEt_3	198.9	1081	ca 5	10.7	5041
Br	Ph	PEt_3	200.6	1058	3.3		
I	Ph	PEt_3	205.7	1014			
			205.4	999			
Cl	Ph	PMe_2Ph	198.7	1063	ca 4	-15.0	5180
Cl	Et	PMe_2Ph[b]	204.2	995		-12.0	5396
Cl	Ph	$PMePh_2$[c]	197.5	1044	4.5	-3.3	5321
Br	Ph	$PMePh_2$				-3.0	5280
						-3.5	5397
I	Ph	$PMePh_2$				-4.4	5016
						-5.1	ca 5100
SCH_2Ph	Ph	$PMePh_2$				-3.8	4048
Cl	Me	$PMePh_2$	199.6			-1.2	
Cl	Et	$PMePh_2$[d]	202.8	973		-1.2	5559
Cl	Ph	PPh_3	196.1	1030	ca 4	11.0	5495
			197.4	1029	ca 4		
Cl	Ph	PCy_3				22.4	5055

(a) spectra were recorded in $CDCl_3$ solution at 25°C

(b) at -40°C two ^{13}C resonances were observed: δC 205.7 ppm, ^1J(Pt-C) 992 Hz; δC 207.0 ppm, ^1J(Pt-C) 982 Hz

(c) δPt -15.3 ppm, obtained from the ^1H-{^{31}P} n.m.r. spectrum

(d) at -40°C two ^{13}C resonances were observed: δC 204.3 ppm, ^1J(Pt-C) 975 Hz; δC 206.2 ppm, ^1J(Pt-C) 955 Hz

^{31}P n.m.r. data for the complexes $[Pt_2(\mu\text{-}X)_2Ph_2L_2]$[a]

X	L	δP/ppm	$^1J(Pt\text{-}P)$/Hz	isomer (%)
Cl	PEt_3	9.0	4757	trans (84)
		8.5	4775	cis (16)
Br	PMe_2Ph	-13.2	4817	trans (72)
		-13.4	4835	cis (28)
Cl	$PMePh_2$[b]	-1.1	5010	trans (70)
		-0.9	5050	cis (30)
I	$PMePh_2$	-0.7	4581	trans (71)
		-0.9	ca 4600	cis (29)
Cl	PPh_3	13.1	5165	trans (75)
		13.6	c	cis (25)

(a) spectra were recorded in $CDCl_3$ solution at 25°C

(b) trans-isomer: $^3J(Pt\text{-}P)$ -10.6 Hz, $|^4J(P\text{-}P)|$ 3.2 Hz, $|^2J(Pt\text{-}Pt)|$ 119 Hz

cis-isomer: $^3J(Pt\text{-}P)$ -15.7 Hz, $|^4J(P\text{-}P)| \leqslant 2$ Hz, $|^2J(Pt\text{-}Pt)|$ 57 Hz

(c) too weak to be observed due to the sparingly soluble nature of the complex

Table 19

reasonable that the bridging thiolate ligand should weaken the Pt-P bond, and hence reduce $^{1}J(Pt-P)$, to the greatest extent. Similarly, $^{1}J(Pt-C)$ values for the complexes $[Pt_2(\mu-X)_2(COPh)_2(PEt_3)_2]$ (X = Cl, Br or I) decrease as the bridging chloride is replaced by bromide and then iodide (Table 18).

The large $^{1}J(Pt-P)$ values do not depend on the existence of halide bridges only, since values of 3931 Hz, 4010 Hz and 4105 Hz were found for the complexes $[Pt_2(\mu-Cl)_2Cl_2L_2]$ (L = PMe_2Ph, $PMePh_2$ and PPh_3, respectively), and the lower value of 3759 Hz for $[Pt_2(\mu-Br)_2Br_2(PMe_2Ph)_2]$. It has been suggested that the high trans-influence of terminal organic groups could cause bridge-weakening and thus affect the values of $^{1}J(Pt-P)$.[193] An alternative explanation, however, is that these variations may reflect the differing cis-influences of terminal organic and halide ligands, as large changes in $^{1}J(Pt-P)$ have been observed for mononuclear complexes on changing the nature of one of the cis-ligands.[177]

The complexes $[Pt_2(\mu-X)_2Ph_2L_2]$ all show two ^{31}P resonances at ambient temperature, while most of the acyl- and aroylplatinum dimers give rise to one broadened signal. The complexes $[Pt_2(\mu-X)_2(COPh)_2(PMePh_2)_2]$ (X = Br or I) exhibit two sharp signals at room temperature, but only on cooling to -40°C are two signals observed for the chloride-bridged acyl- or aroylplatinum derivatives. The ^{13}C n.m.r. spectra of $[Pt_2(\mu-I)_2(COPh)_2(PEt_3)_2]$ and $[Pt_2(\mu-Cl)_2(COPh)_2(PPh_3)_2]$ show two signals at room temperature, but resolution of the two ^{13}C resonances for the other acyl- or aroylplatinum complexes necessitates cooling of their solutions to about -40°C. The observation of two signals is due to the existence of cis- and trans-isomers, and there is now considerable evidence that complexes of the type $[Pt_2(\mu-X)_2Y_2(PR_3)_2]$ (Y = halide, alkyl, aryl, acyl or aroyl) exist in solution as mixtures of cis- and trans-isomers.[193,202]

It is found that trans-isomers usually greatly predominate for the tetrahalide complexes, $[Pt_2(\mu\text{-}X)_2X_2(PR_3)_2]$, while for Y = alkyl or aryl the cis-isomers are readily observed. In fact, in the case of the methylplatinum complex, $[Pt_2(\mu\text{-}Cl)_2Me_2(PMe_2Ph)_2]$, dipole moment measurements suggested that only the cis-isomer was present.[201] Interconversion of the two isomers occurs readily in solution, as evidenced by the line broadening in their n.m.r. spectra, so their ratios adjust rapidly in different solvents. It is likely that only one isomer is obtained on crystallisation, since an X-ray structure determination of the complex $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ revealed that only the trans-isomer was isolated (see chapter 6).

The ^{31}P n.m.r. spectra of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ in CD_2Cl_2, $CDCl_3$ and d_8-toluene were recorded at -40°C. The ratio of the two isomers changed from 3:1 in CD_2Cl_2, to 4:1 in $CDCl_3$ and 7:1 in C_7D_8. Since the major isomer is favoured by the less polar solvent, it is tentatively assigned the trans-configuration.[202] The $^1J(Pt\text{-}P)$ values display some solvent dependence (Table 20), being reduced in the more polar solvents, as was found for the complex trans-$[PtCl_2(PBu^n_3)_2]$.[268] (The cis-$[PtCl_2(PBu^n_3)_2]$ complex, however, showed the reverse trend.[268]) In any given solvent, the cis-dimer exhibits a $^1J(Pt\text{-}P)$ coupling constant which is 115 to 135 Hz greater than that of the trans-form.

The other relevant coupling constants were obtained for the complex $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ by examination of the complete proton-decoupled ^{31}P n.m.r. spectrum. Since two platinum nuclei are present within halide-bridged dimers, three magnetic isomers are possible (corresponding to complexes containing 0, 1 or 2 ^{195}Pt nuclei), and a total of 19 lines should be observed.[250] The magnetic isomer with both platinum nuclei having I = 0 gives rise to a single, intense line (A), while the second magnetic isomer gives rise to

^{31}P n.m.r. data for $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, recorded at -40°C

solvent	dipole moment (debyes)	δP/ppm	^1J(Pt-P)/Hz	δP/ppm	^1J(Pt-P)/Hz	ratio
		trans-complex		cis-complex		
$CDCl_3$	1.15	-11.5	5310	-11.6	5425	4:1
CD_2Cl_2 [a]	1.59	-11.7	5316	-12.2	5445	3:1
C_7D_8	0.40	-11.6	5403	-11.2	5538	7:1

(a) trans-isomer: ^3J(Pt-P) -5.6 Hz, $|^4J$(P-P)| 2.9 Hz, $|^2J$(Pt-Pt)| 152 Hz

cis-isomer: ^3J(Pt-P) -11.0 Hz, $|^4J$(P-P)|<1 Hz, $|^2J$(Pt-Pt)| ca 180 Hz

Table 20

an AA'X pattern (O) from which $^{1}J(Pt-P)$, $^{3}J(Pt-P)$ and $^{4}J(P-P)$ are readily obtained. The third magnetic isomer, containing two ^{195}Pt nuclei, produces an AA'XX' pattern (X) from which $^{2}J(Pt-Pt)$ may be calculated (Figure 5).[284] The separation of lines 3 and 16 (or 4

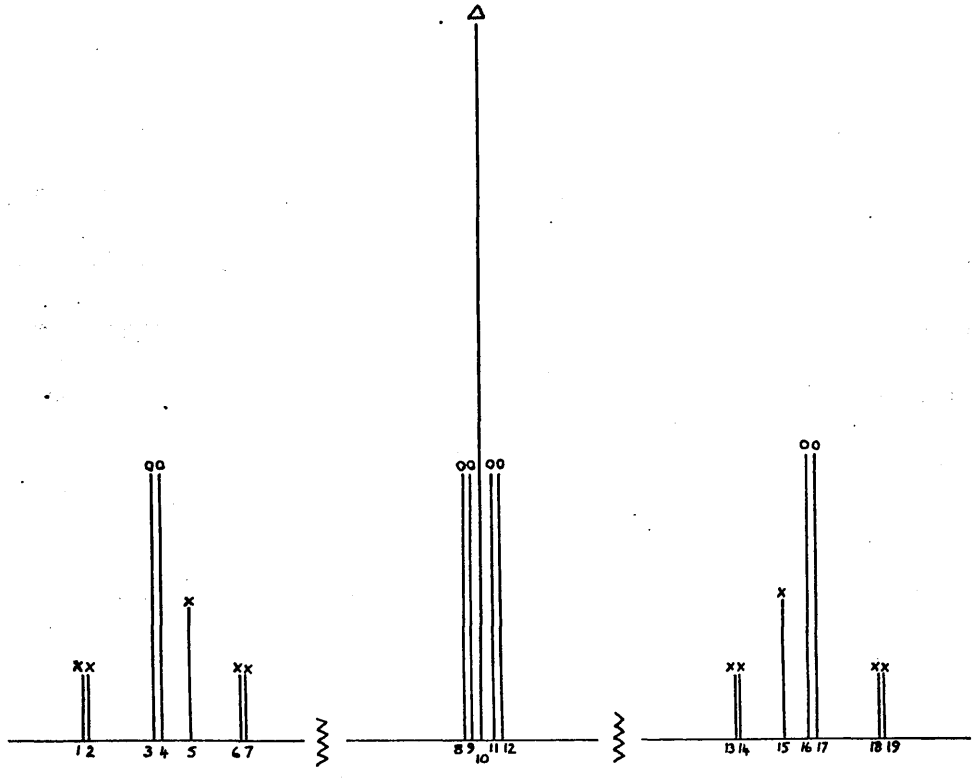


Figure 5

and 17) gives $^{1}J(Pt-P)$, that of 3 and 4, for example, gives $|^{4}J(P-P)|$, while the separation of lines 8 and 11 (or 9 and 12) gives $|^{3}J(Pt-P)|$. The quantities $|^{4}J(P-P) + {}^{2}J(Pt-Pt)|$ and $|^{4}J(P-P) - {}^{2}J(Pt-Pt)|$ are given by the separations of the lines 1 and 7 (or 13 and 19) and the lines 2 and 6 (or 14 and 18), or vice-versa. Thus the magnitudes of the two coupling constants may be obtained separately. Also, the separation of lines 5 and 15 is equal to $|^{1}J(Pt-P) + {}^{3}J(Pt-P)|$, so if these lines fall inside the $^{1}J(Pt-P)/^{4}J(P-P)$ doublet of doublets (3,4 and 16,17) as shown (Figure 5), then $^{1}J(Pt-P)$ and $^{3}J(Pt-P)$ are of opposite sign.

All of the above coupling constants for the complex $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ are given in Table 20, being obtained for the complex in CD_2Cl_2 solution at -40°C. The signs of the $^1J(Pt\text{-}P)$ coupling constants were taken to be positive,[272] and the $^3J(Pt\text{-}P)$ coupling constants were therefore found to be negative. Thus the magnitudes of $^1J(Pt\text{-}P)$ and $^3J(Pt\text{-}P)$ were found to be greater in the cis-complex.

A similar treatment of the ^{31}P n.m.r. spectrum of the complex $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$, recorded in $CDCl_3$ solution at ambient temperature, was performed. The coupling constants are given in Table 19, large $^1J(Pt\text{-}P)$ values being observed for both isomers, and the magnitudes of $^1J(Pt\text{-}P)$ and $^3J(Pt\text{-}P)$ were again greater for the same isomer. This was therefore assigned a cis-configuration, by analogy with the above treatment of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$. Thus it is the trans-isomer of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ which predominates in solution (as was found for the propionyl complex) and, on the basis of the magnitudes of the $^1J(Pt\text{-}P)$ coupling constants, tentative assignments of cis- and trans-geometries for the other $[Pt_2(\mu\text{-}X)_2Ph_2L_2]$ complexes have been made. In each case, therefore, the trans/cis ratio is in the region of 3:1.

This is in contrast to the assignments suggested by Eaborn et al for a series of complexes of the type $[Pt_2(\mu\text{-}Cl)_2R_2L_2]$ (R = aryl or aroyl; L = PEt_3, PMe_2Ph, PPr_3 or PEt_2Ph).[193] They assigned the larger $^1J(Pt\text{-}P)$ coupling constant to the trans-isomer by comparison with the spectra of the complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$. Thus, they suggested that the cis-complex nearly always predominated,[193] as had previously been found for the complex $[Pt_2(\mu\text{-}Br)_2Ph_2(PPr_3)_2]$ from dipole moment measurements.[285] This leads to a direct conflict over the assignment of the cis- and trans-forms of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PEt_3)_2]$, which is the only complex common to both series.

The complex $[Pt_2(\mu\text{-}Cl)_2(C_6H_4Me\text{-}\underline{p})_2(PEt_2Ph)_2]$ shows, for the isomer assigned a cis-configuration by Eaborn,[193] the following coupling constants: $^2J(Pt\text{-}Pt)$ 110 Hz, $^3J(Pt\text{-}P)$ -5 Hz and $^4J(P\text{-}P)$ <3 Hz. These values are closely related to those found for the trans-form of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PMePh_2)_2]$ (Table 19).

It is believed that the assignments made here for the complexes $[Pt_2(\mu\text{-}X)_2R_2L_2]$ (R = phenyl, aroyl or acyl), on the basis of the solvent-dependence of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, are entirely reasonable. The complexes with terminal organic groups all exhibit $^1J(Pt\text{-}P)$ values of about 5000 Hz while the complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$, used as a basis for assignment of configuration by Eaborn,[193] do not have such large values. Thus, it seems reasonable that comparison of the spectra of the complexes $[Pt_2(\mu\text{-}X)_2R_2L_2]$ with those of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ would be the more significant attempt to generalise the assignment of configuration in halide-bridged, organoplatinum complexes.

CHAPTER SIX

Cis- and Trans-Influence of Ligands in Platinum(II) Complexes

Introduction.

The phenomenon of trans-influence has been investigated using several experimental techniques, including vibrational spectroscopy, nuclear magnetic resonance spectroscopy, nuclear quadrupole resonance spectroscopy and photoelectron spectroscopy.[92] The use of X-ray crystallography, however, undoubtedly gives rise to the most accurate measure of bond order and hence, provided a suitable trans-influence model is available, the least ambiguous trans-influence series.

Current theories of trans-influence assume that the phenomenon originates from the σ-bonding in the metal-ligand system, and that it is transmitted throughout the σ-bonding framework of the molecule.[90-92,96,286] Such theories have successfully predicted high trans-influences for hydride and alkyl ligands, for which strong σ-donor and virtually no π-acceptor properties exist. It is conceded, however, that for ligands with π-acceptor properties the trans-influence may also depend on metal-ligand π-backbonding.[286,287] Indeed, the extent of platinum-carbon multiple bonding, for a number of carbon-donor ligands, has been suggested to affect the length of the trans platinum-chlorine bond.[93] To obtain an unambiguous measure of trans-influence from bond length data, it is clearly necessary to study a series of complexes in which as many parameters as possible are kept constant.

Cis- and trans-influence in the complexes cis-$[PtCl_2(PEt_3)L]$.

Crystallographic studies of the complexes cis-$[PtCl_2(PEt_3)L]$, where L = Cl^-,[288] PEt_3,[289] PF_3,[290] CNPh,[291] $C(NPhCH_2)_2$[175] or C(OEt)NHPh,[174] had previously been carried out. The Pt-P and Pt-Cl bond lengths and ^1J(Pt-P) coupling constants are given in Table 21.

In order to further extend this series the complexes cis-$[PtCl_2(PEt_3)L]$, where L = CO, $P(OPh)_3$ or $P(NMe_2)_3$, were prepared,

and their crystal structures were determined by Drs. K.W. Muir and Lj. Manojlovic-Muir in this department.[177,292,293] The complex

L	Pt-P/Å	Pt-Cl/Å (cis to L)	Pt-Cl/Å (trans to L)	^1J(Pt-P)/Hz	Ref.
Cl^-	2.215(4)	2.382(4)	2.301(3)[a]	3704	288
PEt_3	2.259(2)[a]	2.361(6)[a]	2.361(6)[a]	3515	289
PF_3	2.272(3)	2.357(3)	2.305(3)	2760	290
CNPh	2.238(8)	2.365(11)	2.333(12)	3049	291
$C(NPhCH_2)_2$	2.234(3)	2.381(3)	2.362(3)	-	175
C(OEt)NHPh	2.239(8)	2.367(7)	2.361(5)	-	174

(a) mean value

Table 21

cis-$[PtCl_2(PEt_3)(SeEt_2)]$ was also prepared for this purpose, but its crystal structure has not yet been determined. The platinum-ligand bond lengths and ^1J(Pt-P) coupling constants for the complexes cis-$[PtCl_2(PEt_3)L]$ (L = CO, $P(OPh)_3$ or $P(NMe_2)_3$) are given in Table 22.

L	Pt-P/Å (L)	Pt-Cl/Å (trans to L)	Pt-P/Å (PEt_3)	Pt-Cl/Å (trans to PEt_3)	^1J(Pt-P)/Hz (PEt_3)	Ref.
CO	-	2.296(4)	2.265(3)	2.368(3)	2793	177
$P(OPh)_3$	2.182(2)	2.344(2)	2.269(1)	2.355(2)	3210[a]	292
$P(NMe_2)_3$	2.236(9)	2.368(11)	2.285(9)	2.375(9)	3515[b]	293

(a) $P(OPh)_3$, ^1J(Pt-P) 6255 Hz

(b) $P(NMe_2)_3$, ^1J(Pt-P) 5023 Hz

Table 22

The ligands L in Tables 21 and 22 include both strong and weak σ-donors, such as PEt_3 and Cl^- respectively, and strong and weak π-acceptors, such as CO and carbene ligands respectively. Thus, with such an extensive array of related complexes available, examination of the dependence of metal-ligand bonding on the nature of L is possible.

The Pt-Cl (trans to L) bond lengths in Tables 21 and 22, which ought to provide a measure of the trans-influence of L since the cis-ligands remain unchanged, range from 2.296 Å to 2.368 Å and increase along the following series:

$$CO \sim Cl^- \simeq PF_3 < CNPh \leq P(OPh)_3 < PEt_3 \sim C(NPhCH_2)_2 \sim C(OEt)NHPh \sim P(NMe_2)_3$$

This series reflects the increasing σ-basicity and decreasing π-acidity of the ligands, and is therefore compatible with current theories of trans-influence in transition metal complexes.[92,93,96,286]

What is perhaps more surprising, in view of the concentration hitherto on the role of trans-influence, is that the effects of L on the platinum-ligand bonds cis to itself are also significant, though the operation of this cis-influence is apparently less simple. The Pt-P bond lengths range from 2.215 Å for L = Cl^- to 2.285 Å for L = $P(NMe_2)_3$, such a variation being of a similar magnitude to that produced in the Pt-Cl (trans to L) bonds. The variation in Pt-Cl (cis to L) distances is smaller, covering a range of about 0.03 Å. Additionally, it is found that the variations in Pt-P and Pt-Cl distances (both cis to L) are inversely related; that is, a ligand L which causes a decrease in the Pt-P distance also produces an increase in the Pt-Cl bond length. The platinum-phosphorus distances, which show the greater variation on changing the cis-ligand L, increase in the following order:

$$Cl^- < C(NPhCH_2)_2 \sim CNPh \sim C(OEt)NHPh < PEt_3 \sim CO \sim P(OPh)_3 \sim PF_3 \leqslant P(NMe_2)_3$$

The order of increasing Pt-Cl (cis to L) distance is approximately the reverse of this series.

The cis-influence of ligands L may be due to their steric or electronic properties. In sterically crowded platinum complexes, lengthening of platinum-phosphorus bonds to relieve steric repulsions has been observed. Thus, for example, the Pt-P bond distances in trans-$[PtI_2(PCy_3)_2]$ are 2.371 Å,[294] while those in trans-$[PtBr_2(PEt_3)_2]$ are 2.315 Å.[95] This difference of nearly 0.06 Å was attributed to the greater inter-ligand repulsions in the former.[294] The steric interactions within the cis-$[PtCl_2(PEt_3)L]$ complexes would be expected to be much weaker, however, and it is noted that the observed cis-influence series bears little relationship to the size of the ligands L as given, for example, by Tolman's cone angle measurements.[209] Furthermore, it might reasonably be expected that increasing bulk of L would result in greater Pt-P and Pt-Cl (cis to L) distances. The negative correlation between Pt-P and Pt-Cl (cis to L) distances cannot readily be explained on the basis of steric demand, so it may be concluded that the cis-influence of L is predominantly an electronic effect.

It is also clear from the bond length data in Tables 21 and 22 that the cis- and trans-influences of L are not related to each other, since the Pt-P and Pt-Cl (cis to L) distances show no correlation with the Pt-Cl (trans to L) bond lengths. This is indicative of transmission of cis- or trans-influences occurring through different electronic mechanisms within the molecular framework. That strong σ-donor ligands are generally of high trans-influence is emphasised by current theories,[92,93,96,284] and it is

clear that the ordering of the ligands L in the cis-influence series is not related to their σ-basicities. This is consistent with the theory of Syrkin,[295] which considers that interactions between mutually cis σ-bonds are of little importance, though the calculations of Zumdahl and Drago predicted, in contrast, that cis- and trans-influences operating through the σ-bonding system should be of comparable magnitude.[96]

It has been suggested that $^{1}J(Pt-P)$ coupling constants are a measure of the s-character within the platinum-phosphorus bond,[90,181] and it may be seen that both $^{1}J(Pt-P)$ and the Pt-P distance are sensitive to the nature of the cis-ligand L (Tables 21 and 22). No clear correlation between the two parameters is evident, however. Where L = PEt_3 or CO, for example, the Pt-P bonds are of equal length (to within experimental error) but the $^{1}J(Pt-P)$ values for the two complexes differ by 722 Hz. Thus, although the s-character and overall strength of the Pt-P bond are sensitive to the nature of the cis-ligand, no correlation between the two is obvious.

It may be observed that, for the ligands L, those ligands which occur at the upper end of the cis-influence series are those which are considered to be strong π-acids, such as CO and PF_3. Conversely, ligands of poor π-acceptor ability, such as Cl^- and carbene ligands, occupy positions at the lower end of the series. Such observations suggest that the cis-influence of L may be related to its π-acidity. The lengthening of the Pt-P bonds may then be due to competition between PEt_3 and L for the metal d_π-electrons. The shortening of the Pt-Cl (cis to L) bonds may result from increased Pt→L π-backdonation, leading to greater electrostatic attraction between the chloride ligand and the metal, or may occur indirectly by modification of the trans-influence of the phosphine.

Thus, while the mode of operation of trans-influence is

apparently fairly well understood, being transmitted via the σ-bonding network, the phenomenon of cis-influence has been less extensively studied. The above discussion, however, strongly suggests that the π-bonding system is important for the transmission of the cis-influence. Finally, since the Pt-P bond is more sensitive to the nature of the cis-ligands than is the Pt-Cl bond, it should be noted that the use of platinum-phosphorus bond lengths, coupling constants or stretching frequencies as a measure of trans-influence will only be valid where the cis-ligands are kept constant.

Crystal structure of the complex trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$.

Although the complex $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ exists in solution as a mixture of cis- and trans-isomers, slow crystallisation from CH_2Cl_2/Et_2O produced colourless crystals of the trans-form. The crystal structure of trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ was determined in this department by Drs. K.W. Muir and Lj. Manojlovic-Muir, and a view of the molecule is shown in Figure 6. Selected bond lengths and angles are given in Table 23. The Pt_2Cl_2 unit is

	bond length (Å)		bond angle (deg)
Pt-P	2.209(1)	Cl-Pt-Cl'	83.7(1)
Pt-C(1)	1.972(5)	Cl-Pt-P	97.4(1)
Pt-Cl	2.498(1)	Cl-Pt-C(1)	174.9(1)
Pt-Cl'	2.393(1)	Cl'-Pt-P	178.8(1)
		Cl'-Pt-C(1)	91.2(1)
		P-Pt-C(1)	87.6(1)
		Pt-Cl-Pt'	96.3(1)

Table 23

exactly planar, and the bond lengths and angles within the PMe_2Ph

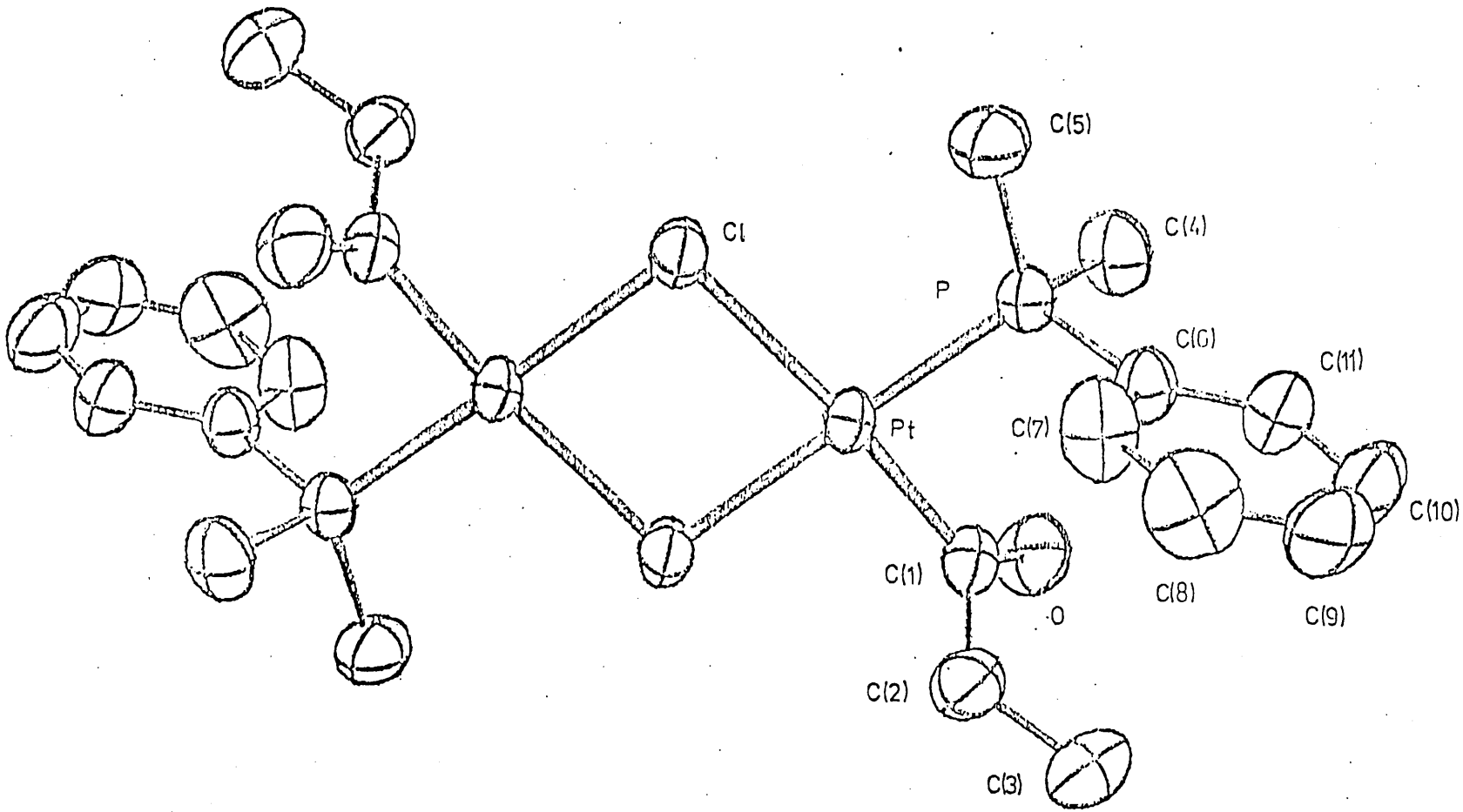


Figure 6

ligand are unexceptional, though a short intramolecular Pt⋯H contact of 2.8 Å exists for one hydrogen atom attached to C(2).

Two points of interest emerge from the bond length data obtained. Firstly, although both cis- and trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$ exhibit large $^1J(Pt\text{-}P)$ coupling constants (Table 20), the Pt-P distance is only slightly shorter than those generally found for mononuclear tertiary phosphine complexes of platinum(II) (Tables 21 and 22). It is, in fact, almost identical to that found in the $[PtCl_3(PEt_3)]^-$ anion, which has a $^1J(Pt\text{-}P)$ value of 3704 Hz.[288] This is over 1500 Hz smaller than that in trans-$[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, and these observations suggest that the proposed correlation between Pt-P coupling constants and bond lengths[181] is only valid, at best, where comparisons involve complexes which do not differ so greatly in structure.

Secondly, the bridging Pt-Cl bond lengths trans to PMe_2Ph and COEt differ by ca 0.10 Å (Table 23), and such a difference suggests that the σ-propionyl group exerts a considerably greater trans-influence on the bridging bonds. This difference is more marked than in mononuclear complexes, where Pt-Cl distances are commonly within the ranges 2.35 to 2.38 Å when trans to tertiary phosphine (Tables 21 and 22), and 2.40 to 2.42 Å when trans to σ-carbon donors.[93]

Crystallographic studies of a number of trans-$[Pt_2(\mu\text{-}Cl)_2X_2Y_2]$ complexes have been performed, and the bridging Pt-Cl distances are given in Table 24. Although each bridging chlorine atom participates in Pt-Cl bonds which are trans to two different terminal ligands, there is apparently no significant relationship between the two Pt-Cl distances for a given chlorine atom. Instead, each Pt-Cl distance appears to be determined by the terminal ligand, the Pt-Cl distances increasing in the following trans-ligand order:

$$Cl^- < \pi\text{-}C{=}C < AsMe_3 \lessapprox PR_3 < \sigma\text{-}C$$

Apart from the relative magnitudes of the trans-influences of tertiary phosphines and σ-carbon donors, this series parallels exactly that derived for mononuclear complexes.[92,93,286]

complex	X	Y	Pt-Cl(Å) (trans to X)	Pt-Cl(Å) (trans to Y)	Ref.
$[Pt_2Cl_6]^{2-}$	Cl	Cl	2.318	2.330	296
	Cl	Cl	2.337	2.327	
$[Pt_2Cl_4\{CH_2C(OMe)_2\}_2]$	σ-C	Cl	-	2.324(7)	297
$[Pt_2Cl_4(C_5H_8)_2]$	π-C=C	Cl	2.349(5)	2.320(5)	298
$[Pt_2Cl_4(C_7H_{12})_2]$	π-C=C	Cl	2.362(6)	2.328(6)	298
$[Pt_2Cl_4(CMe_2{=}C{=}CMe_2)_2]$	π-C=C	Cl	2.382(5)	2.342(5)	299
$[Pt_2Cl_4(PPr^n_3)_2]$	PPr^n_3	Cl	2.425(8)	2.315(8)	300
$[Pt_2Cl_4(AsMe_3)_2]$	$AsMe_3$	Cl	2.394(6)	2.312(5)	301
$[Pt_2Cl_2(C_{11}H_{15}O)_2]$	σ-C	π-C=C	2.51	2.34	302
$[Pt_2Cl_2(C_6H_4N{=}NPh)_2]$	σ-C	N	2.460(5)	2.326(6)	303
$[Pt_2Cl_2(Bu^t_2PCH_2CMe_2CH_2)_2]$	σ-C	Bu^t_2P-	2.460	2.402	304
$[Pt_2Cl_2(COEt)_2(PMe_2Ph)_2]$	σ-C	PMe_2Ph	2.498(1)	2.393(1)	

Bond lengths in trans-$[Pt_2(\mu\text{-}Cl)_2X_2Y_2]$ complexes

Table 24

Conclusions.

From the above studies three important points emerge in relation to trans-influence investigations. Firstly, the exceptionally high $^1J(Pt\text{-}P)$ values in halide-bridged platinum dimers do not reflect

very short Pt-P bond distances. Hence, secondly, comparative data involving bond lengths or coupling constants can only be meaningful when complexes of the same type are being studied. Thirdly, the role of cis-ligands is more important than had perhaps previously been imagined, with bond length variations of similar magnitudes being caused by a change of cis- or trans-ligand in certain cases.

Experimental.

cis-Dichloro(carbonyl)triethylphosphineplatinum:

$[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ (5.758g, 7.50 mmol) was dissolved in warm toluene ($200cm^3$). Carbon monoxide was passed through the solution for ca 2 h until it had become almost colourless. White crystals precipitated, and were separated by filtration, and the solvent was removed from the remaining solution. Recrystallisation from hot ethanol gave cis-$[PtCl_2(CO)(PEt_3)]$ as colourless crystals (3.429g, 56%), m.pt. 134-136°C (lit. value[55] 134-136°C).

cis-Dichloro(triethylphosphine)triphenylphosphiteplatinum:

Triphenylphosphite (1 mol equiv) was added to a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ in sym-tetrachloroethane. The solution became colourless, and a large volume of n-pentane was added to precipitate the product. This was crystallised from warm acetone to give colourless crystals of cis-$[PtCl_2(PEt_3)\{P(OPh)_3\}]$, m.pt. 188-189°C. (Found: C 41.76, H 4.42, P 8.75% Calculated for $C_{24}H_{30}Cl_2O_3P_2Pt$: C 41.50, H 4.32, P 8.93%)

cis-Dichloro(triethylphosphine)tris(dimethylamino)phosphineplatinum:

$[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ (0.373g, 0.49 mmol) was dissolved in warm toluene ($20cm^3$). Tris(dimethylamino)phosphine ($0.20cm^3$, 1.16 mmol) was added and the solution became intense yellow-green. The hot solution was filtered and allowed to cool slowly, by packing the flask in cotton wool. This resulted in precipitation of long, colourless needles of cis-$[PtCl_2(PEt_3)\{P(NMe_2)_3\}]$, m.pt. 197-199°C.

(Found: C 26.40, H 6.19, N 7.80, P 11.85% Calculated for $C_{12}H_{33}Cl_2N_3P_2Pt$: C 26.33, H 6.08, N 7.68, P 11.33%)

cis-Dichloro(triethylphosphine)diethylselenideplatinum:

$[Pt_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_2]$ (3.45g, 4.49 mmol) was dissolved in chloroform ($100cm^3$) under nitrogen. Diethylselenide (1.23g, 8.98 mmol) was added and the solution was stirred for 24 h. The solvent was removed and the cream-coloured residue was dried *in vacuo*. Upon crystallisation from $CHCl_3/Et_2O$, cis-$[PtCl_2(PEt_3)(SeEt_2)]$ was obtained as colourless crystals, m.pt. 119-122°C. (Found: C 23.22, H 4.74, Cl 13.79% Calculated for $C_{10}H_{25}Cl_2PPtSe$: C 23.04, H 4.84, Cl 13.61%)

In solution, cis- and trans-isomers were detected by ^{31}P n.m.r. spectroscopy, although assignment of the n.m.r. signals to the geometric isomers was not possible: δP 5.8 p.p.m., $^1J(Pt\text{-}P)$ 3401 Hz and δP 9.3 p.p.m., $^1J(Pt\text{-}P)$ 3315 Hz, in the ratio 4:3.

Di-μ-chlorodipropionylbis(dimethylphenylphosphine)diplatinum:

cis-$[PtCl_2(CO)(PMe_2Ph)]$ (1.29g, 2.98 mmol) was suspended in benzene ($50cm^3$) and diethylmercury ($0.32cm^3$, 3.01 mmol) was added. After 1 h the black solution was filtered, the solvent was removed, and the residue was pumped to remove traces of unreacted $HgEt_2$. Ethylmercuric chloride was removed by sublimation at 55°C/0.001 torr for 48 h. The remaining solid was crystallised from benzene/n-pentane, then from methylene chloride/diethyl ether to yield colourless crystals of $[Pt_2(\mu\text{-}Cl)_2(COEt)_2(PMe_2Ph)_2]$, m.pt. 136-138°C. (Found: C 31.18, H 3.75, Cl 8.80% Calculated for $C_{22}H_{32}Cl_2O_2P_2Pt_2$: C 31.02, H 3.79, Cl 8.34%)

References.

1. W.C. Zeise, Pogg. Ann., 1827, 9, 632; idem., ibid., 1831, 21, 497.
2. E. Frankland, Annalen, 1849, 17, 213; idem., J. Chem. Soc., 1850, 2, 263.
3. G.B. Buckton, Proc. Roy. Soc., 1859, 9, 309.
4. V. Grignard, Compt. rend., 1900, 130, 1322.
5. W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, Ber. Chem. Gesellschaft, 1914, 47, 473.
6. K. Ziegler and H. Colonius, Annalen, 1930, 479, 135.
7. W.J. Pope and S.J. Peachey, Proc. Chem. Soc., 1907, 23, 86; idem., J. Chem. Soc., 1909, 571.
8. W.J. Pope and C.S. Gibson, J. Chem. Soc. Trans., 1907, 91, 2061.
9. T.J. Kealy and P.L. Pauson, Nature, 1951, 168, 1039; S.A. Miller, J.A. Tebboth, and J.F. Tremaine, J. Chem. Soc., 1952, 632.
10. G. Wilkinson, M. Rosenblum, M.C. Whiting, and R.B. Woodward, J. Amer. Chem. Soc., 1952, 74, 2125; E.O. Fischer and W. Pfab, Z. Naturforsch, 7b, 377.
11. S.J. Anderson, J. Chem. Soc., 1934, 971.
12. J. Chatt and R.G. Wilkins, Nature, 1950, 165, 859.
13. J. Chatt, L.M. Vallarino, and L.M. Venanzi, J. Chem. Soc., 1957, 2496.
14. J. Chatt, L.M. Vallarino, and L.M. Venanzi, J. Chem. Soc., 1957, 3413.
15. G. Calvin and G.E. Coates, Chem. and Ind., 1958, 160.
16. (a) J. Chatt and B.L. Shaw, J. Chem. Soc., 1959, 705; (b) idem., ibid., 1959, 4020.
17. For example, J. Halpern, Disc. Faraday Soc., 1968, 46, 7.
18. P. Cossee, J. Catalysis, 1964, 3, 80.

19. A.J. Chalk and R.F. Harrod, Adv. Organometallic Chem., 1968, 6, 119.

20. P.M. Maitlis, "The Organic Chemistry of Palladium", Acad. Press, 1971, vol.II, and references therein.

21. G. Henrici-Olive and S. Olive, Angew. Chemie (Int. Edn.), 1979, 18, 77.

22. For example, R.J. Kokes, Accts. Chem. Res., 1973, 6, 226.

23. M. Orchin, Adv. Catalysis, 1966, 16, 1.

24. J.A. Osborn, F.H. Jardine, J.F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.

25. N. Calderon, Accts. Chem. Res., 1972, 5, 127.

26. K.P.C. Vollhardt, Accts. Chem. Res., 1977, 10, 1.

27. P. Chini, Inorg. Chim. Acta Rev., 1968, 2, 31.

28. N. Kutepov and H. Kindler, Angew. Chemie, 1960, 72, 802.

29. T. Kamijo, T. Kitamura, N. Sakamoto, and T. Joh, J. Organometallic Chem., 1973, 54, 265.

30. R.A. Sanchez-Delgado, J.S. Bradley, and G. Wilkinson, J.C.S. Dalton, 1976, 399.

31. N.V. Sidgwick, "The Electronic Theory of Valence", Oxford Univ. Press, London, 1929, p.163.

32. P.S. Braterman and R.J. Cross, Chem. Soc. Rev., 1973, 2, 271.

33. For example, E. Singleton, J. Organometallic Chem., 1978, 158, 413.

34. C.A. Tolman, W.C. Seidel, and D.H. Gerloch, J. Amer. Chem. Soc., 1972, 94, 2669.

35. E.H. Brooks and R.J. Cross, Organometallic Chem. Rev. (A), 1970, 6, 227.

36. D.P. Rice and J.A. Osborn, J. Organometallic Chem., 1971, 30, C84.

37. C.A. Tolman, Chem. Soc. Rev., 1972, 1, 337.

38. M.L.H. Green and R. Mahtab, J.C.S. Dalton, 1979, 262; J.X. McDermott, M.E. Wilson, and G.M. Whitesides, J. Amer. Chem. Soc., 1976, 98, 6529.

39. F.G.N. Cloke and M.L.H. Green, J.C.S. Chem. Comm., 1979, 127.

40. R.J. Cross and R. Wardle, J. Chem. Soc. (A), 1971, 2000.

41. J. Chatt and G.J. Leigh, Angew. Chemie (Int. Edn.), 1978, 17, 400.

42. J.S. Thayer, Organometallic Chem. Rev. (A), 1970, 5, 53.

43. R.S. Nyholm and P. Royo, Chem. Comm., 1969, 421.

44. J.K. Stille and K.S.Y. Lau, Accts. Chem. Res., 1977, 10, 434.

45. F.R. Hartley, "The Chemistry of Platinum and Palladium", App. Sci. Publ., London, 1973.

46. R. Ugo, Coord. Chem. Rev., 1968, 3, 319.

47. A. Sen and J. Halpern, J. Amer. Chem. Soc., 1977, 99, 8337.

48. R.F. Heck et al, J. Organic Chem., 1978, 43, 2941 and following papers.

49. T. Yoshida, Y. Ueda, and S. Otsuka, J. Amer. Chem. Soc., 1978, 100, 3941.

50. G.C. Bond, Disc. Faraday Soc., 1966, 41, 200; R. Ugo, G. La Monica, S. Cenini, A. Segre, and F. Conti, J. Chem. Soc. (A), 1971, 522.

51. J.M. Davidson and C. Triggs, J. Chem. Soc. (A), 1968, 1324.

52. D.C.L. Perkins, R.J. Puddephatt, and C.F.H. Tipper, J. Organometallic Chem., 1979, 166, 261.

53. F.R. Hartley, Organometallic Chem. Rev. (A), 1970, 6, 119.

54. J. Chatt and L.M. Venanzi, J. Chem. Soc., 1955, 3858; idem., ibid., 1957, 2445.

55. J. Chatt, N.P. Johnson, and B.L. Shaw, J. Chem. Soc., 1964, 1662.

56. B. Crociani and R.L. Richards, J. Organometallic Chem., 1978, 154, 65.

57. R.P. Stewart and P.M. Treichel, J. Amer. Chem. Soc., 1970, 92, 2710.

58. S.J. Ashcroft and C.T. Mortimer, J. Chem. Soc. (A), 1967, 930.

59. Lj. Manojlovic-Muir, K.W. Muir, and R. Walker, J.C.S. Dalton, 1976, 1279.

60. B. Jovanovic and Lj. Manojlovic-Muir, J.C.S. Dalton, 1972, 1176.

61. B. Jovanovic, Lj. Manojlovic-Muir, and K.W. Muir, J.C.S. Dalton, 1974, 195.

62. E.M. Badley, K.W. Muir, and G.A. Sim, J.C.S. Dalton, 1976, 1930.

63. F.R. Hartley, Chem. Rev., 1969, 69, 799.

64. J. Chatt and L.A. Duncanson, J. Chem. Soc., 1953, 2939.

65. D.B. Powell and N. Sheppard, J. Chem. Soc., 1960, 2519.

66. J. Chatt, R.G. Guy, and L.A. Duncanson, J. Chem. Soc., 1961, 827.

67. E.O. Greaves and P.M. Maitlis, J. Organometallic Chem., 1966, 6, 104.

68. J.F. Richardson and N.C. Payne, Can. J. Chem., 1977, 55, 3203.

69. A. Evans, C.T. Mortimer, and R.J. Puddephatt, J. Organometallic Chem., 1975, 85, 101.

70. G.R. Davies, W. Hewertson, R.H.B. Mais, P.G. Owston, and C.G. Patel, J. Chem. Soc. (A), 1970, 1873.

71. H.C. Clark and L.E. Manzer, J. Organometallic Chem., 1973, 59, 411.

72. A. Segnitz, E. Kelly, S.H. Taylor, and P.M. Maitlis, J. Organometallic Chem., 1977, 124, 113.

73. J.D. Smith and J.D. Oliver, Inorg. Chem., 1978, 17, 2585.

74. P.S. Manchand, H.S. Wong, and J.F. Blount, J. Organic Chem., 1978, 43, 4769; B.M. Trost and T.R. Verhoeven, J. Amer. Chem. Soc., 1978, 100, 3435.

75. D.F. Pollock and P.M. Maitlis, J. Organometallic Chem., 1971, 26, 407.

76. D.B. Crump and N.C. Payne, Inorg. Chem., 1973, 12, 1663.

77. K.K. Cheung, R.J. Cross, K.P. Forrest, R. Wardle, and M. Mercer, J.C.S. Chem. Comm., 1971, 875.

78. J.X. McDermott, J.F. White, and G.M. Whitesides, J. Amer. Chem. Soc., 1973, 95, 4451; idem., ibid., 1976, 98, 6521.

79. G.B. Young and G.M. Whitesides, J. Amer. Chem. Soc., 1978, 100, 5808.

80. P.S. Braterman, J.C.S. Chem. Comm., 1979, 70.

81. P.M. Maitlis, Pure Appl. Chem., 1973, 33, 489.

82. K. Moseley and P.M. Maitlis, J.C.S. Dalton, 1974, 169.

83. J.T. van Gemert and P.R. Wilkinson, J. Phys. Chem., 1964, 68, 645.

84. M. Green, G. Scholes, and F.G.A. Stone, J.C.S. Dalton, 1978, 309.

85. R.D. Cramer, E.L. Jenner, R.V. Lindsey Jr., and U.G. Stolberg, J. Amer. Chem. Soc., 1963, 85, 1691.

86. J.H. Flynn and H.M. Hulburt, J. Amer. Chem. Soc., 1954, 76, 3393.

87. R.F. Heck, J. Amer. Chem. Soc., 1968, 90, 5518 and following papers.

88. F. Basolo and R.G. Pearson, Prog. Inorg. Chem., 1962, 4, 381.

89. F.R. Hartley, Chem. Soc. Rev., 1973, 2, 163.

90. A. Pidcock, R.E. Richards, and L.M. Venanzi, J. Chem. Soc. (A), 1966, 1707.

91. L.M. Venanzi, Chem. Brit., 1968, 4, 162.

92. T.G. Appleton, H.C. Clark, and L.E. Manzer, Coord. Chem. Rev., 1973, 10, 335.

93. Lj. Manojlovic-Muir and K.W. Muir, Inorg. Chim. Acta, 1974, 10, 47.

94. P.G. Owston, J.M. Partridge, and J.M. Rowe, Acta Crystallogr., 1960, 13, 246.

95. G.G. Messmer and E.L. Amma, Inorg. Chem., 1966, 5, 1775.

96. S.S. Zumdahl and R.S. Drago, J. Amer. Chem. Soc., 1968, 90, 6669.

97. F. Basolo and R.G. Pearson, "Mechanism of Inorganic Reactions", Wiley, New York, 2nd edn., 1967, ch.5.

98. P. Haake and R.M. Pfeiffer, Chem. Comm.,1969, 1330.

99. D.G. Cooper and J. Powell, J. Amer. Chem. Soc., 1973, 95, 1102.

100. J.H. Price, J.P. Birk, and B.B. Wayland, Inorg. Chem., 1978, 17, 2245.

101. G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, J. Chem. Soc. (A), 1971, 1877.

102. R. Romeo, P. Uguagliati, and U. Belluco, J. Mol. Catalysis, 1975/76, 1, 325.

103. R.J. Mureinik, Coord. Chem. Rev., 1978, 25, 1.

104. D.T. Rosevear and F.G.A. Stone, J. Chem. Soc., 1965, 5275.

105. C.D. Cook and G.S. Jauhal, Can. J. Chem., 1967, 45, 301.

106. (a) J.D. Ruddick and B.L. Shaw, J. Chem. Soc. (A), 1969, 2801; (b) idem., ibid., 1969, 2964.

107. J.D. Ruddick and B.L. Shaw, Chem. Comm., 1967, 1135.

108. J. Kuyper, Inorg. Chem., 1977, 16, 2171; idem., ibid., 1978, 17, 77.

109. I.M. Blacklaws, L.C. Brown, E.A.V. Ebsworth, and F.J.S. Reed, J.C.S. Dalton, 1978, 877.

110. M.J. Mays, R.N.F. Simpson, and F.P. Stefanini, J. Chem. Soc. (A), 1970, 3000.

111. H.B. Lee and P.M. Maitlis, J.C.S. Chem. Comm., 1974, 601.

112. G.E. Coates and C. Parkin, J. Chem. Soc., 1963, 421.

113. M.P. Brown, R.J. Puddephatt, and C.E.E. Upton, J.C.S. Dalton, 1974, 2457.

114. P.S. Braterman, R.J. Cross, and G.B. Young, J.C.S. Dalton, 1977, 1892.

115. A. Shiotani and H. Schmidbaur, J. Organometallic Chem., 1972, 37, C24.

116. E.H. Brooks, R.J. Cross, and F. Glockling, Inorg. Chim. Acta, 1968, 2, 17.

117. J.K. Jawad and R.J. Puddephatt, J.C.S. Chem. Comm., 1977, 892.

118. G.M. Whitesides, J.F. Gaasch, and E.R. Stedronsky, J. Amer. Chem. Soc., 1972, 94, 5258.

119. G.M. Whitesides, E.R. Stedronsky, C.P. Casey, and J. San Fillipo, 1970, 92, 1426.

120. J. Chatt and B.L. Shaw, J. Chem. Soc., 1962, 5075.

121. (a) F.S. Dyachkovsky and N.E. Khrushch, Zh. Obshch. Chim. U.S.S.R., 1971, 41, 1779; (b) A.S. Khachaturov, L.S. Breslov, and I.Y. Paddubnyi, J. Organometallic Chem., 1972, 42, C18.

122. N.J. Cooper and M.L.H. Green, J.C.S. Chem. Comm., 1974, 761.

123. K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green, and R. Mahtab, J.C.S. Chem. Comm., 1978, 604.

124. A.J. Cheney, B.E. Mann, B.L. Shaw, and R.M. Slade, Chem. Comm., 1970, 1176.

125. G.W. Parshall, Accts. Chem. Res., 1970, 3, 139.

126. M.A. Bennett and D.L. Milner, J. Amer. Chem. Soc., 1969, 91, 6983.

127. W. Keim, J. Organometallic Chem., 1968, 14, 179; idem., ibid., 1969, 19, 161.

128. H. Takahashi and J. Tsuji, J. Organometallic Chem., 1967, 10, 511.

129. A.A. Kiffen, C. Masters, and L. Raynand, J.C.S. Dalton, 1975, 853.

130. G.M. Whitesides, D.E. Bergbreiter, and P.E. Kendall, J. Amer. Chem. Soc., 1974, 96, 2806.

131. M.F. Lappert and B. Prokai, Adv. Organometallic Chem., 1967, 5, 225.

132. R.F. Heck, Accts. Chem. Res., 1969, 2, 10.

133. G.P. Chiusoli, Accts. Chem. Res., 1973, 6, 422.

134. A. Wojcicki, Adv. Organometallic Chem., 1974, 12, 31.

135. F. Calderazzo and K. Noack, Coord. Chem. Rev., 1966, 1, 118.

136. A. Wojcicki, Adv. Organometallic Chem., 1973, 11, 87.

137. F. Calderazzo, Angew. Chemie (Int. Edn.), 1977, 16, 299.

138. A. Wojcicki, Accts. Chem. Res., 1971, 4, 344.

139. Y. Yamamoto and H. Yamazaki, Coord. Chem. Rev., 1972, 8, 225.

140. For example, D.M. Roundhill, Adv. Organometallic Chem., 1975, 13, 273.

141. M.H. Chisholm and H.C. Clark, Accts. Chem. Res., 1973, 6, 202.

142. T.H. Coffield, J. Kozikowski, and R.D. Closson, J. Organic Chem., 1957, 22, 598.

143. K. Noack and F. Calderazzo, J. Organometallic Chem., 1967, 10, 101.

144. (a) G. Booth and J. Chatt, Proc. Chem. Soc., 1961, 67;
(b) idem., J. Chem. Soc. (A), 1966, 634.

145. H. Berke and R. Hoffmann, J. Amer. Chem. Soc., 1978, 100, 7224.

146. D.L. Thorn and R. Hoffmann, J. Amer. Chem. Soc., 1978, 100, 2079.

147. H.C. Clark, C. Jablonski, J. Halpern, A. Mantovani, and T.A. Weil, Inorg. Chem., 1974, 13, 1541.

148. H.C. Clark and C. Jablonski, Inorg. Chem., 1974, 13, 2213.

149. H.C. Clark and C.S. Wong, J. Amer. Chem. Soc., 1974, 96, 7213.

150. R. Ros, R.A. Michelin, R. Bataillard, and R. Roulet, J. Organometallic Chem., 1979, 165, 107.

151. H.C. Clark and C.S. Wong, J. Organometallic Chem., 1975, 92, C31; H.C. Clark, P.L. Fiess, and C.S. Wong, Can. J. Chem., 1977, 55, 177, 189.

152. H.C. Clark and R.J. Puddephatt, Inorg. Chem., 1971, 10, 18; T.G. Appleton, M.H. Chisholm, and H.C. Clark, J. Amer. Chem. Soc., 1972, 94, 8912.

153. H.C. Clark and C.S. Wong, J. Amer. Chem. Soc., 1977, 99, 7073.

154. D.E. James, L.F. Hines, and J.K. Stille, J. Amer. Chem. Soc., 1976, 98, 1806; D.E. James and J.K. Stille, J. Amer. Chem. Soc., 1976, 98, 1810.

155. L. Chugaev and M. Skanavy-Grigorizeva, J. Russ. Chem. Soc., 1915, 47, 776.

156. W.M. Butler and J.H. Enemark, Inorg. Chem., 1971, 10, 2416.

157. D.J. Cardin, B. Cetinkaya, and M.F. Lappert, Chem. Rev., 1972, 72, 545.

158. E.O. Fischer, Pure Appl. Chem., 1972, 30, 353.

159. F.A. Cotton and C.M. Lukehart, Prog. Inorg. Chem., 1973, 16, 487.

160. M.F. Lappert, J. Organometallic Chem., 1975, 100, 139.

161. E.O. Fischer, Adv. Organometallic Chem., 1976, 14, 1.

162. D.J. Cardin, B. Cetinkaya, M.J. Doyle, and M.F. Lappert, Chem. Soc. Rev., 1973, 2, 99.

163. C.P. Casey and T.J. Burkhardt, J. Amer. Chem. Soc., 1974, 96, 7808.

164. C.P. Casey and W.R. Brunsvold, Inorg. Chem., 1977, 16, 391; C.P. Casey, L.D. Albin, and T.J. Burkhardt, J. Amer. Chem. Soc., 1977, 99, 2533; C.P. Casey, S.H. Bertz, and T.J. Burkhardt, Tetrahedron Lett., 1973, 1421.

165. E.O. Fischer, G. Kreis, C.G. Kreiter, J. Muller, G. Huttner, and H. Lorenz, Angew. Chemie (Int. Edn.), 1973, 12, 564.

166. E.O. Fischer, R.L. Clough, G. Besl, and F.R. Kreissl, Angew. Chemie (Int. Edn.), 1976, 15, 543.

167. D.J. Cardin, B. Cetinkaya, M.F. Lappert, Lj. Manojlovic-Muir, and K.W. Muir, J.C.S. Chem. Comm., 1971, 400.

168. E.M. Badley, J. Chatt, and R.L. Richards, J. Chem. Soc. (A), 1971, 21.

169. M.H. Chisholm and H.C. Clark, Inorg. Chem., 1971, 10, 1711.

170. A.L. Balch, J. Organometallic Chem., 1972, 37, C19.

171. M.H. Chisholm and H.C. Clark, Chem. Comm., 1971, 1484.

172. J.S. Miller and A.L. Balch, Inorg. Chem., 1972, 11, 2069.

173. B. Jovanovic, Lj. Manojlovic-Muir, and K.W. Muir, J.C.S. Dalton, 1974, 195.

174. E.M. Badley, K.W. Muir, and G.A. Sim, J.C.S. Dalton, 1976, 1930.

175. Lj. Manojlovic-Muir and K.W. Muir, J.C.S. Dalton, 1974, 2427.

176. B.Jovanovic, Lj. Manojlovic-Muir, and K.W. Muir, J. Organometallic Chem., 1971, 33, C75.

177. Lj. Manojlovic-Muir, K.W. Muir, and T. Solomun, J. Organometallic Chem., 1977, 142, 265.

178. R.A. Bell, M.H. Chisholm, D.A. Couch, and L.A. Rankel, Inorg. Chem., 1977, 16, 677.

179. M.H. Chisholm and H.C. Clark, J. Amer. Chem. Soc., 1972, 94, 1532.

180. S.O. Grim, R.L. Keiter, and W. McFarlane, Inorg. Chem., 1967, 6, 1133.

181. G.G. Mather, A. Pidcock, and G.J.N. Rapsey, J.C.S. Dalton, 1973, 2095.

182. J.M. Jenkins and B.L. Shaw, J. Chem. Soc. (A), 1966, 770.

183. F.A. Cotton and V.W. Day, J.C.S. Chem. Comm., 1974, 415; F.A. Cotton, T. Latour, and A.G. Stanislovski, J. Amer. Chem. Soc., 1974, 96, 754.

184. M.J. Bennett, P.B. Donaldson, P.B. Hitchcock, and R. Mason, Inorg. Chim. Acta, 1975, 12, L9.

185. M.H. Chisholm, H.C. Clark, W.S. Johns, J.E.H. Ward, and K. Yasufuku, Inorg. Chem., 1975, 14, 900.

186. R.J. Cross and R. Wardle, J. Chem. Soc. (A), 1970, 840.

187. C. Eaborn, N. Farrell, J.L. Murphy, and A. Pidcock, J.C.S. Dalton, 1976, 58.

188. R. Schmutzler, Adv. Fluorine Chem., 1965, 5, 31.

189. D. Forster, J. Amer. Chem. Soc., 1976, 98, 846.

190. C.W. Bird, Chem. Rev., 1962, 62, 283.

191. P.E. Garrou and R.F. Heck, J. Amer. Chem. Soc., 1976, 98, 4115.

192. R.W. Glyde and R.J. Mawby, Inorg. Chem., 1971, 10, 854.

193. C. Eaborn, K.J. Odell, and A. Pidcock, J.C.S. Dalton, 1978, 1288.

194. M. Kubota, R.K. Rothrock, and J. Geibel, J.C.S. Dalton, 1973, 1267.

195. R.J. Irving and E.A. Magnusson, J. Chem. Soc., 1956, 1860.

196. H.C. Clark, K.R. Dixon, and W.J. Jacobs, Chem. Comm., 1968, 93.

197. M.J. Church and M.J. Mays, Chem. Comm., 1968, 435.

198. A.C. Smithies, M. Rycheck, and M. Orchin, J. Organometallic Chem., 1968, 12, 199.

199. F.H. Allen and A. Pidcock, J. Chem. Soc. (A), 1968, 2700.

200. W.J. Cherwinski, B.F.G. Johnson, J. Lewis, and J.R. Norton, J.C.S. Dalton, 1975, 1156.

201. R.J. Puddephatt and P.J. Thompson, J.C.S. Dalton, 1977, 1219.

202. C. Crocker and P.L. Goggin, J. Chem. Research, 1978, (S) 93, (M) 1274.

203. C.J. Wilson, M. Green, and R.J. Mawby, J.C.S. Dalton, 1974, 1293.

204. S.J. Ashcroft, A. Maddock, and G. Beech, J.C.S. Dalton, 1974, 462.

205. C.J. Wilson, M. Green, and R.J. Mawby, J.C.S. Dalton, 1974, 421.

206. D. Wright, Chem. Comm., 1966, 197; E. Lodewijk and D. Wright, J. Chem. Soc. (A), 1968, 119.

207. R.J. Cross and J. Gemmill, personal communication.

208. M. Kubota, D.M. Blake, and S.A. Smith, Inorg. Chem., 1971, 10, 1430.

209. C.A. Tolman, Chem. Rev., 1977, 77, 313.

210. G. Ferguson, P.J. Roberts, E.C. Alyea, and M. Khan, Inorg. Chem., 1978, 17, 2965.

211. C.A. Tolman, J. Amer. Chem. Soc., 1970, 92, 2953.

212. D.A. Duddell, P.L. Goggin, R.J. Goodfellow, M.G. Norton, and J.G. Smith, J. Chem. Soc. (A), 1970, 545.

213. T.P. Cheeseman, A.L. Odell, and H.A. Raethel, Chem. Comm., 1968, 1496.

214. M.J. Church and M.J. Mays, J. Chem. Soc. (A), 1970, 1938.

215. D.M. Adams, J. Chatt, J. Gerratt, and A.D. Westland, J. Chem. Soc., 1964, 734.

216. A.W. Cooke, B.Sc. Thesis, University of Glasgow, 1971.

217. A. Peloso, Coord. Chem. Rev., 1973, 10, 123.

218. B. Cox, University of Stirling, personal communication.

219. J. Chatt and R.G. Wilkins, J. Chem. Soc., 1952, 273 and 4300; idem., ibid., 1953, 70; idem., ibid., 1956, 525.

220. P. Haake and T.A. Hylton, J. Amer. Chem. Soc., 1962, 84, 3774.

221. J. Chatt, J. Chem. Soc., 1950, 2301.

222. D.A. Redfield and J.H. Nelson, Inorg. Chem., 1973, 12, 15.

223. L. Cattalini and M. Martelli, J. Amer. Chem. Soc., 1969, 91, 312.

224. U. Belluco, M. Martelli, and A. Orio, Inorg. Chem., 1966, 5, 582.

225. P. Haake and R.M. Pfeiffer, J. Amer. Chem. Soc., 1970, 92, 4996.

226. P. Haake and R.M. Pfeiffer, J. Amer. Chem. Soc., 1970, 92, 5243.

227. D.G. Cooper and J. Powell, Can. J. Chem., 1973, 51, 1634.

228. R. Roulet and C. Barbey, Helv. Chim. Acta, 1973, 56, 2179.

229. W.J. Louw, J.C.S. Chem. Comm., 1974, 353.

230. J. Powell and D.G. Cooper, J.C.S. Chem. Comm., 1974, 749.

231. D.A. Redfield and J.H. Nelson, J. Amer. Chem. Soc., 1974, 96, 6219.

232. D.A. Redfield, J.H. Nelson, R.A. Henry, D.W. Moore, and H.B. Jonassen, J. Amer. Chem. Soc., 1974, 96, 6298.

233. A.W. Verstuyft and J.H. Nelson, Inorg. Chem., 1975, 14, 1501; L.M. Knight and J.H. Nelson, Inorg. Chem., 1977, 16, 1317.

234. D.A. Redfield, L.W. Cary, and J.H. Nelson, Inorg. Chem., 1975, 14, 50.

235. W.J. Louw, Inorg. Chem., 1977, 16, 2147.

236. R.G. Pearson, W.J. Louw, and J. Rajaram, Inorg. Chim. Acta, 1974, 9, 251.

237. W.J. Louw, D.J.A. de Waal, and G.J. Kruger, J.C.S. Dalton, 1976, 2364.

238. R. Romeo, Inorg. Chem., 1978, 17, 2040.

239. G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, Inorg. Chem., 1969, 8, 2207; idem., ibid., 1970, 9, 1525.

240. V. Ricevuto, R. Romeo, and M. Trozzi, J.C.S. Dalton, 1972, 1857.

241. V. Ricevuto, R. Romeo, and M. Trozzi, J.C.S. Dalton, 1974, 927.

242. R. Romeo, M.L. Tobe, and M. Trozzi, Inorg. Chim. Acta, 1974, 11, 231.

243. G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, J.C.S. Dalton, 1974, 1377.

244. R. Romeo, D. Minniti, and M. Trozzi, Inorg. Chim. Acta, 1975, 14, L15.

245. R. Romeo, D. Minniti, and M. Trozzi, Inorg. Chem., 1976, 15, 1134.

246. R. Romeo, D. Minniti, and S. Lanza, Inorg. Chim. Acta, 1976, 18, L15.

247. R. van Eldik, D.A. Palmer, and H. Kelm, Inorg. Chem., 1979, 18, 572.

248. A. Tamaki, S.A. Magennis, and J.K. Kochi, J. Amer. Chem. Soc., 1974, 96, 6140.

249. R.G. Pearson and M.M. Muir, J. Amer. Chem. Soc., 1966, 88, 2163.

250. A.A. Kiffen, C. Masters, and J.P. Visser, J.C.S. Dalton, 1975, 1311.

251. A. Saika and C.P. Slichter, J. Chem. Phys., 1954, 22, 26.

252. K.J. Packer, J. Chem. Soc., 1963, 960.

253. F.B. Ogilvie, J.M. Jenkins, and J.G. Verkade, J. Amer. Chem. Soc., 1970, 92, 1916.

254. J.A. Pople and D.P. Santry, Mol. Phys., 1964, 8, 1.

255. P.T. Inglefield and L.W. Reeves, J. Chem. Phys., 1964, 40, 2424.

256. J.G. Verkade, R.W. King, and C.W. Heitsch, Inorg. Chem., 1964, 3, 884.

257. A. Pidcock, R.E. Richards, and L.M. Venanzi, Proc. Chem. Soc., 1962, 184.

258. B.T. Heaton and A. Pidcock, J. Organometallic Chem., 1968, 14, 235.

259. F.H. Allen and S.N. Sze, J. Chem. Soc. (A), 1971, 2054.

260. M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers, and J.E.H. Ward, J. Amer. Chem. Soc., 1973, 95, 8574.

261. H.C. Clark and J.E.H. Ward, J. Amer. Chem. Soc., 1974, 96, 1741.

262. J. Browning, P.L. Goggin, R.J. Goodfellow, M.G. Norton, A.J.M. Rattray, B.F. Taylor, and J. Mink, J.C.S. Dalton, 1977, 2061.

263. B. Crociani and R.L. Richards, J. Organometallic Chem., 1978, 144, 85.

264. C. Eaborn, K.J. Odell, and A. Pidcock, J.C.S. Dalton, 1979, 134.

265. J. Browning, P.L. Goggin, R.J. Goodfellow, N.W. Hurst, L.G. Mallinson, and M. Murray, J.C.S. Dalton, 1978, 872.

266. W. McFarlane, J.C.S. Dalton, 1974, 324.

267. J.D. Kennedy, W. McFarlane, R.J. Puddephatt, and P.J. Thompson, J.C.S. Dalton, 1976, 874.

268. K.R. Dixon, M. Fakley, and A. Pidcock, Can. J. Chem., 1976, 54, 2733.

269. E.G. Finer and R.K. Harris, Prog. N.m.r. Spectroscopy, 1971, 6, 61.

270. J.D. Baldeschwieler and E.W. Randall, Chem. Rev., 1963, 63, 81; R.A. Hoffmann and S. Forsen, Prog. N.m.r. Spectroscopy, 1966, 1, 15.

271. W. McFarlane, Quart. Rev., 1969, 23, 187.

272. W. McFarlane, Chem. Comm., 1967, 772; idem., J. Chem. Soc. (A), 1967, 1922.

273. M.A. Bennett, R. Bramley, and I.B. Tomkins, J.C.S. Dalton, 1973, 166.

274. R. Bramley, J.R. Hall, G.A. Swile, and I.B. Tomkins, Aust. J. Chem., 1974, 27, 2491.

275. I.J. Colquhoun, J.D. Kennedy, W. McFarlane, and R.J. Puddephatt, J.C.S. Chem. Comm., 1975, 638.

276. J.D. Kennedy, W. McFarlane, and R.J. Puddephatt, J.C.S. Dalton, 1976, 745.

277. T. Iwayanagi and Y. Saito, Chem. Lett., 1976, 1193.

278. M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers, and J.E.H. Ward, J. Amer. Chem. Soc., 1975, 97, 721.

279. A.J. Cheney, B.E. Mann, and B.L. Shaw, Chem. Comm., 1971, 431.

280. D.J. Cardin, B. Cetinkaya, E. Cetinkaya, M.F. Lappert, E.W. Randall, and E. Rosenberg, J.C.S. Dalton, 1973, 1982.

281. R.D. Bertrand, F.B. Ogilvie, and J.G. Verkade, J. Amer. Chem. Soc., 1970, 92, 1908.

282. A. Pidcock, R.E. Richards, and L.M. Venanzi, J. Chem. Soc. (A), 1968, 1970.

283. M.H. Chisholm, H.C. Clark, J.E.H. Ward, and K. Yasufuku, Inorg. Chem., 1975, 14, 893.

284. F.A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York and London, 1969, p.117.

285. J. Chatt and J.M. Davidson, J. Chem. Soc., 1964, 2433.

286. R. McWeeny, R. Mason, and A.D.C. Towl, Disc. Faraday Soc., 1969, 47, 20; R. Mason and A.D.C. Towl, J. Chem. Soc. (A), 1970, 1601.

287. L.D. Pettit, Quart. Rev., 1971, 25, 1.

288. G.W. Bushnell, A. Pidcock, and M.A.R. Smith, J.C.S. Dalton, 1975, 572.

289. Lj. Manojlovic-Muir, K.W. Muir, and T. Solomun, unpublished work.

290. P.B. Hitchcock, B. Jacobson, and A. Pidcock, unpublished work.

291. E.M. Badley, Ph.D. Thesis, University of Sussex, 1969.

292. A.N. Caldwell, Lj. Manojlovic-Muir, and K.W. Muir, J.C.S. Dalton, 1977, 2265.

293. A.N. Keith, Lj. Manojlovic-Muir, and K.W. Muir, unpublished work.

294. N.W. Alcock and P.G. Leviston, J.C.S. Dalton, 1974, 1834.

295. Y.K. Syrkin, Bull. Acad. Sci. U.S.S.R., 1948, 69.

296. C.D. Cowman, J.C. Thibeault, R.F. Ziolo, and H.B. Gray, J. Amer. Chem. Soc., 1976, 98, 3209.

297. A. de Renzi, B. di Blasio, G. Paiaro, A. Panunzi, and C. Pedone, Gazz. Chim. Ital., 1976, 106, 765.

298. J. Bordner and D.W. Wertz, Inorg. Chem., 1974, 13, 1639.

299. T.G. Hewitt and J.J. de Boer, J. Chem. Soc. (A), 1971, 817.

300. M. Black, R.H.B. Mais, and P.G. Owston, Acta Crystallogr. B, 1969, 25, 1760.

301. S.F. Watkins, J. Chem. Soc. (A), 1970, 168.

302. W.A. Whitla, H.M. Powell, and L.M. Venanzi, Chem. Comm., 1966, 310.

303. R.C. Elder, R.D.P. Cruea, and R.F. Morrison, Inorg. Chem., 1976, 15, 1623.

304. R. Mason, M. Textor, N. Al-Saleem, and B.L. Shaw, J.C.S. Chem. Comm., 1976, 292.